# $NO_x$ Control & Measurement Technology for Heavy-Duty Diesel Engines

**Project ID: ACS032**


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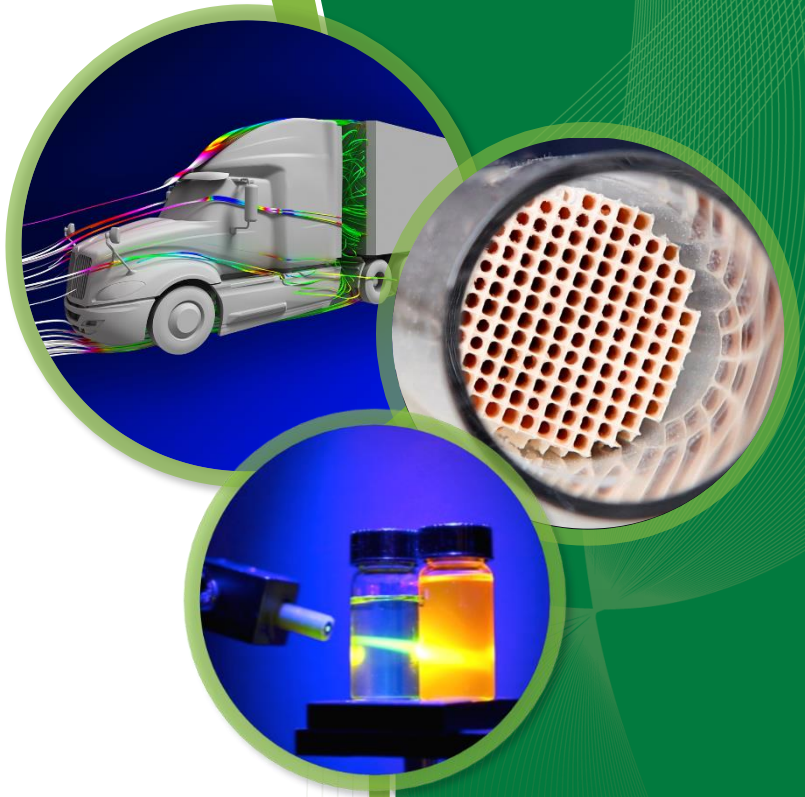


DOE Vehicle Technologies Office
Annual Merit Review & Peer Evaluation Meeting
June 20, 2018; Washington, DC

DOE Managers:
Gurpreet Singh, Ken Howden


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# Overview

## Timeline

- Year 3 of 3-year

## Budget

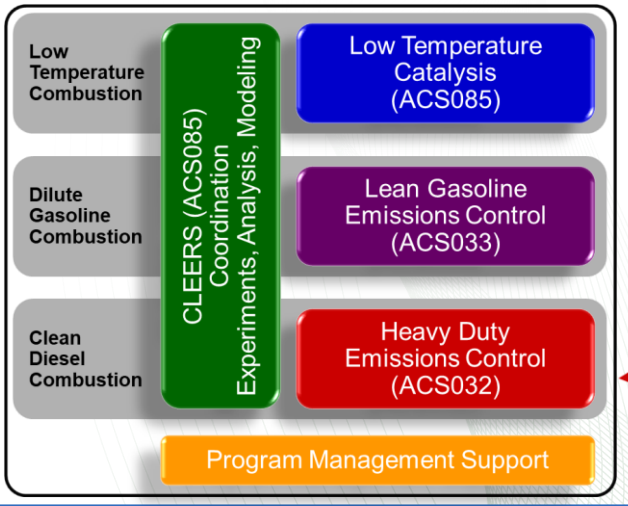
- 1:1 DOE:Cummins cost share
  - In-kind Cummins contribution
- FY18 DOE Funding: $300k
  - Task3: Diesel Emissions Control
  - Part of ORNL project: “Enabling Fuel Efficient Engines by Controlling Emissions” (2015 VTO AOP Lab Call)

## Barriers

- From DOE VT MYPP:
  - 2.3.1.B: Cost-effective emission control
  - 2.3.1.C: Modeling for emission control
  - 2.3.1.E: Emissions-control durability

## Partners

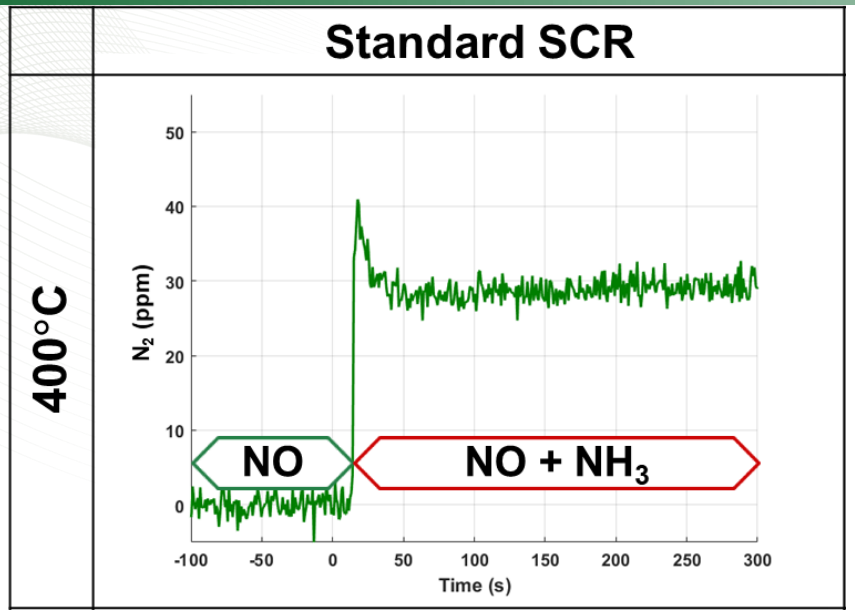
- ORNL & Cummins Inc.

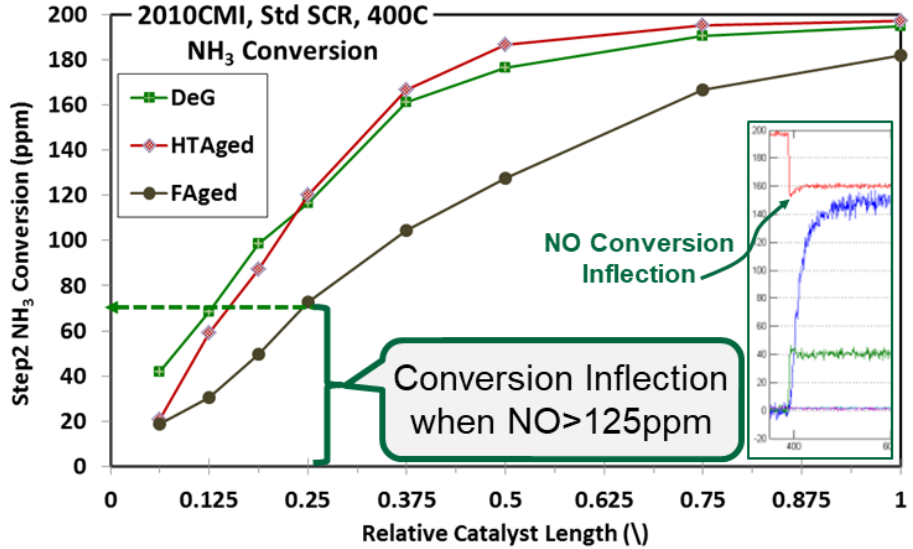


# Milestones

| FY | Qtr | Milestone & Objectives | Status |
|---|---|---|---|
| 2018 | 1 | Demonstrate an experimental method for characterizing relative rates of components steps of a global SCR mechanism | complete |

# Background: Using Transients to Advance Catalyst Technology



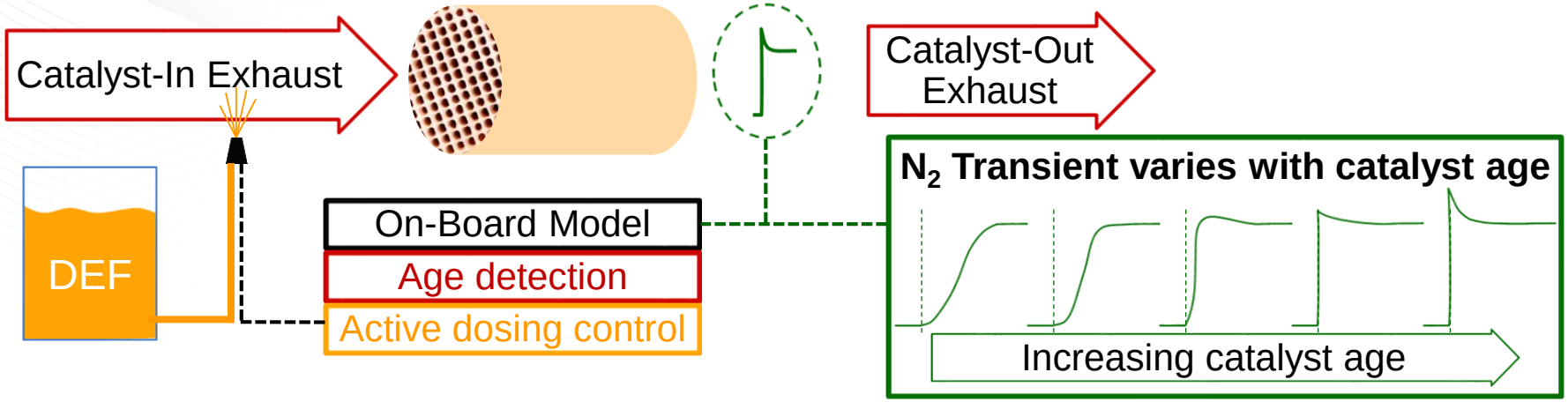




Partridge, et al., 2015 CLEERS Workshop

- Conversion Inflections (CI) can occur with Cu/SCR catalysts at SCR onset
  - Fast conversion onset & Slower conversion degradation to Steady state level
- SCR-onset CI has been observed for different Cu-SCR catalysts
  - Cu-Beta, Cu-CHA
- CI may be useful for monitoring catalyst ageing
  - Systematic CI progression with ageing: axial & transient at fixed axial position
- Not due to $NH_3$-coverage inhibition as with Fe-SCR (see Tech. Backup Slides)
- CI is not captured by predictive Cu-SCR models (shown in FY17 AMR presentation)

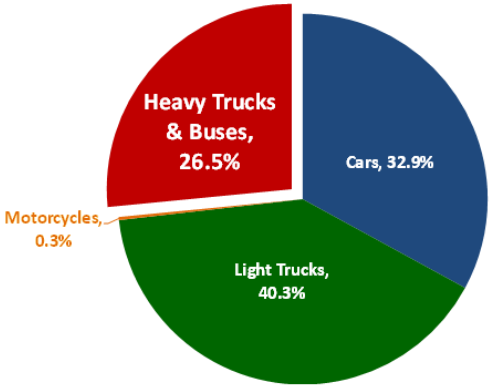
# Objectives

- Improve transient performance of SCR models
- Understand how field ageing impacts SCR reaction network
- Enable aged-state sensing to optimize catalyst performance




# Relevance

- Better catalyst performance allows engine to be optimized for fuel efficiency




On-Highway Petroleum Use
(Source: Transportation Energy Data Book)

**Heavy Duty SCR Durability Standard:**

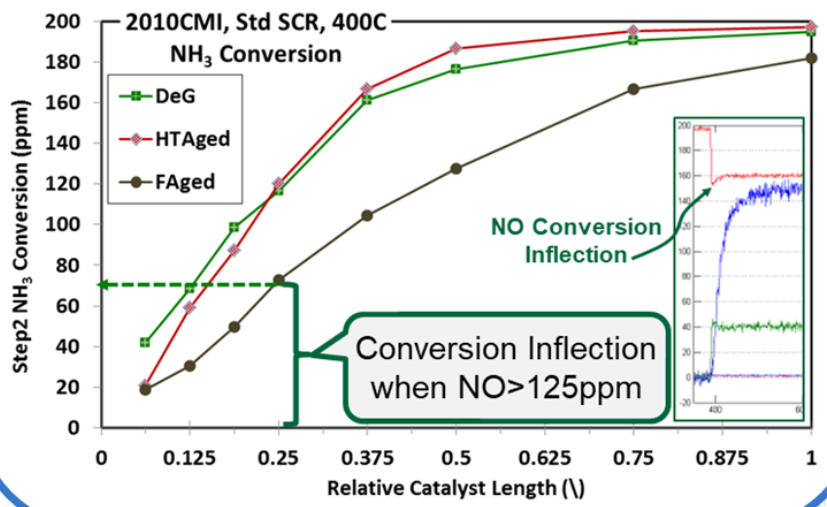
**435,000 miles!**

(Source: EPA)

# Research Path from Observation to Improved Fuel Economy

CI ∝ Aged State

Transient conversion inflections (CI) vary progressively with catalyst age



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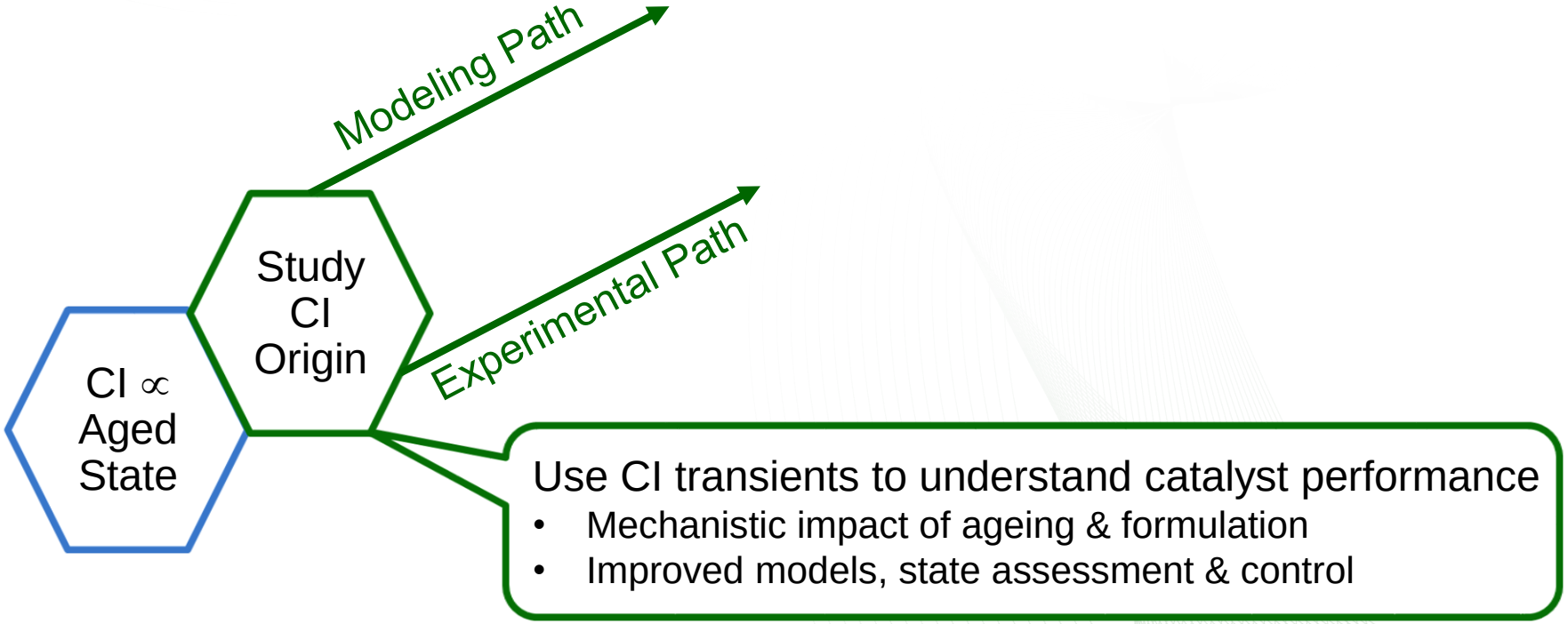
# Research Path from Observation to Improved Fuel Economy



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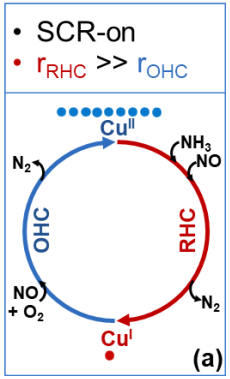
# Research Path from Observation to Improved Fuel Economy

## Formulate SCR Cu-redox model to study transient CI nature




RHC: $Cu^{II}(OH)(NH_3) + 2{\cdot}NH_3 + NO \rightarrow Cu^{I}(NH_3)_2 + N_2 + 2H_2O$

$r_{RHC} = k_{RHC} \cdot [Cu^{II}] \cdot [NO] \cdot (\theta_{NH3})^{\sim 0} \cong k_{RHC} \cdot [Cu^{II}] \cdot [NO]$

OHC: $2{\cdot}Cu^{I}(NH_3)_2 + O_2 + 2{\cdot}NO \rightarrow 2{\cdot}\ Cu^{II}(OH)(NH_3) + 2{\cdot}N_2 + 2{\cdot}H_2O$

$r_{OHC} = k_{OHC} \cdot [Cu^{I}]^2 \cdot [O_2] \cdot [NO]$

Net Standard SCR: $4{\cdot}NO + 4{\cdot}NH_3 + O_2 \rightarrow 4{\cdot}N_2 + 6{\cdot}H_2O$

Kinetic Model

Study CI Origin

CI ∝ Aged State



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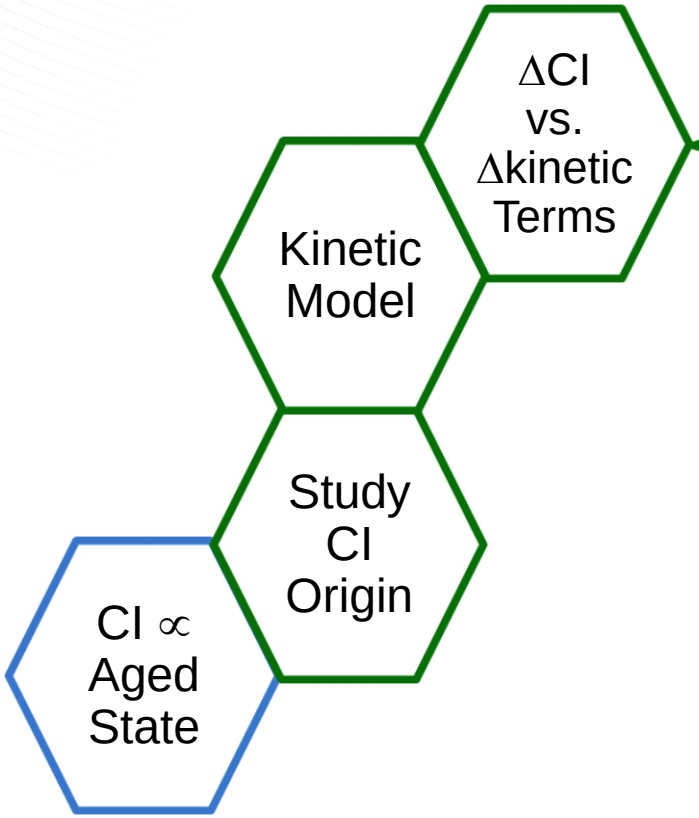
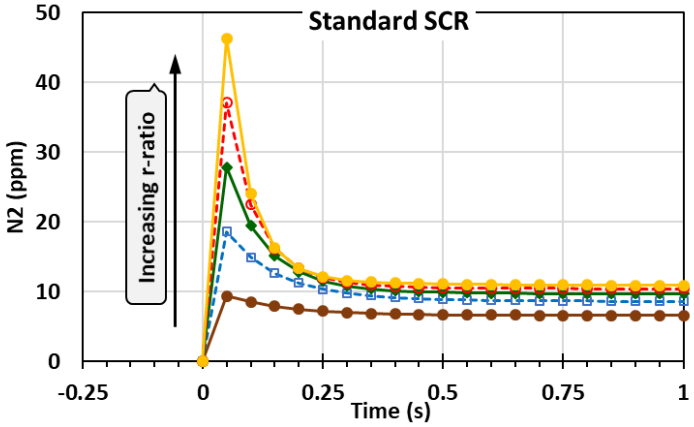
# Research Path from Observation to Improved Fuel Economy




CI transients vary progressively with changes in kinetic parameters



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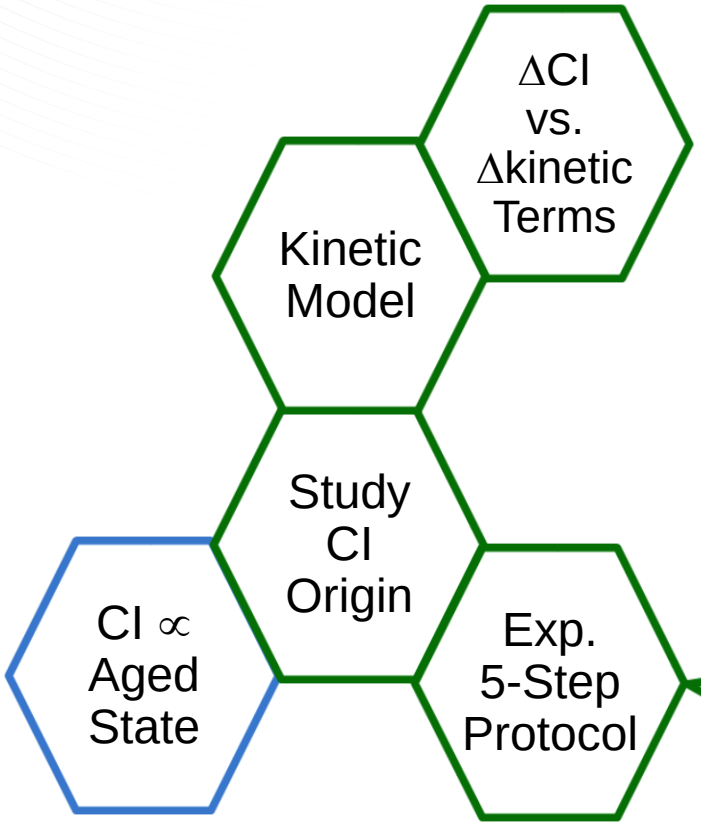
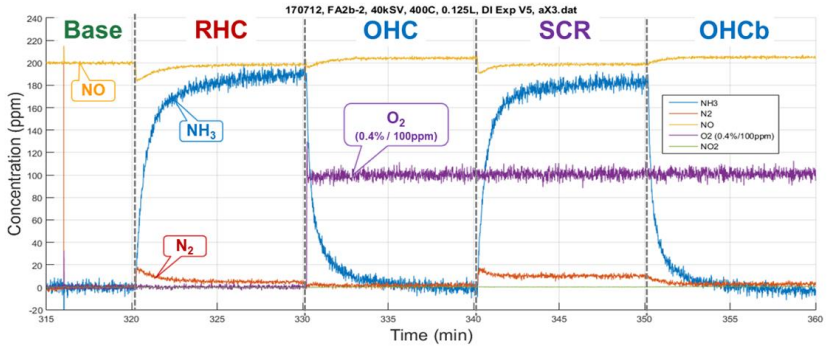
# Research Path from Observation to Improved Fuel Economy




Transient step response of individual & combined Cu-redox half-cycles



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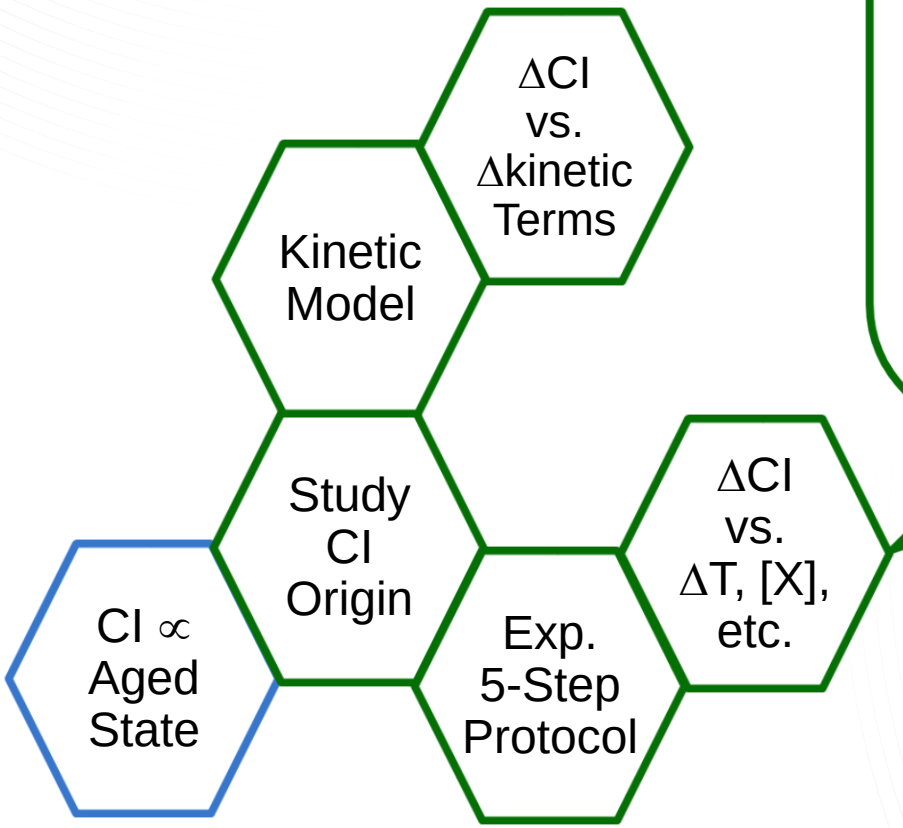
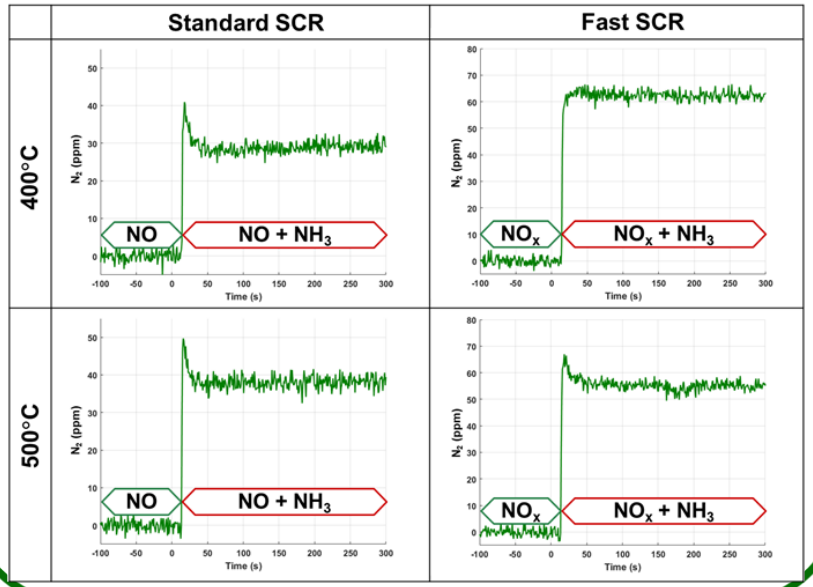
# Research Path from Observation to Improved Fuel Economy




Onset transients vary progressively with environmental conditions



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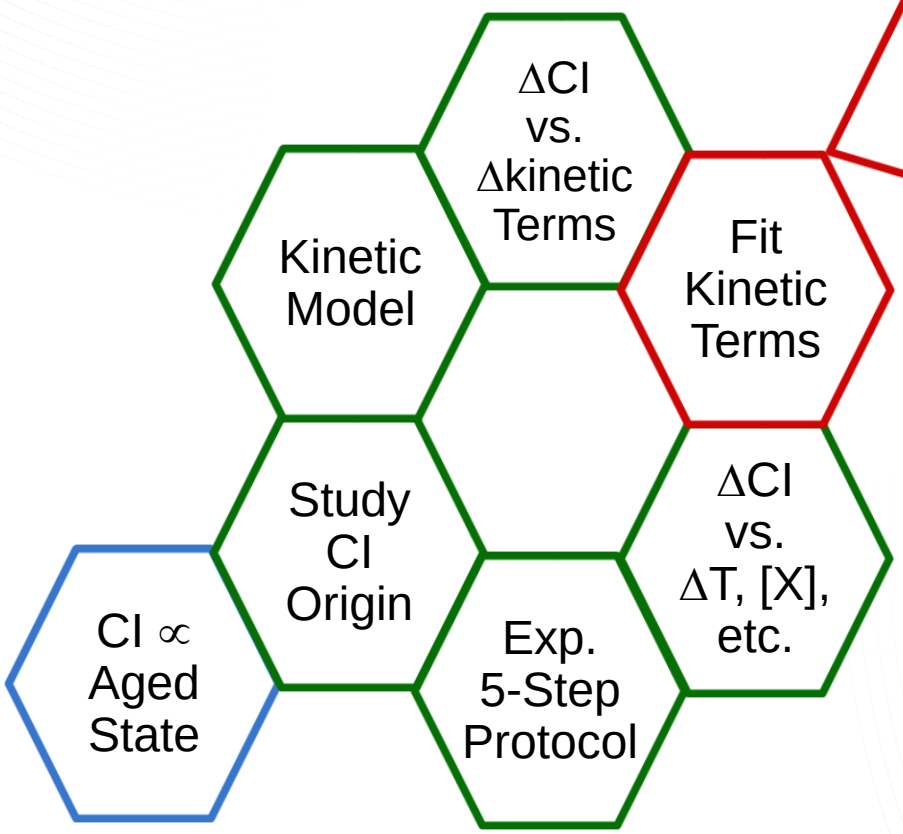
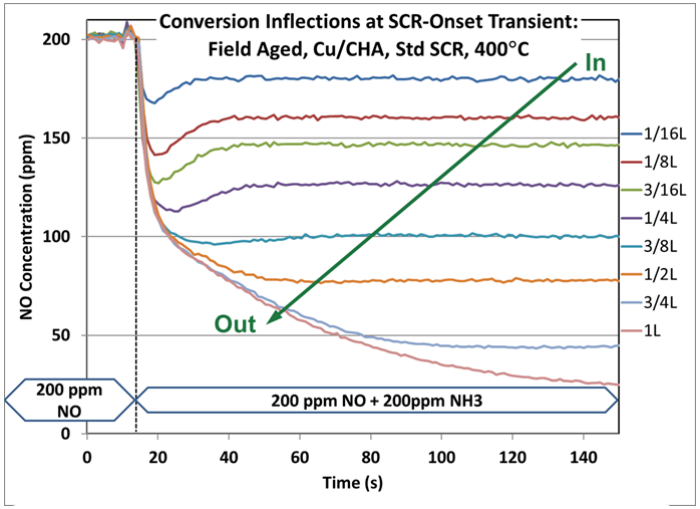
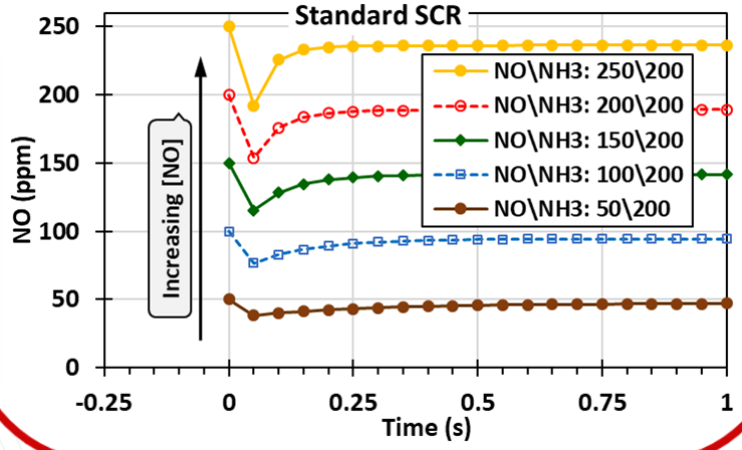
# Research Path from Observation to Improved Fuel Economy




Model & measurements trend

- CI origin relates to Cu half cycles
- Use Exp.-Modeling method to determine kinetic parameters



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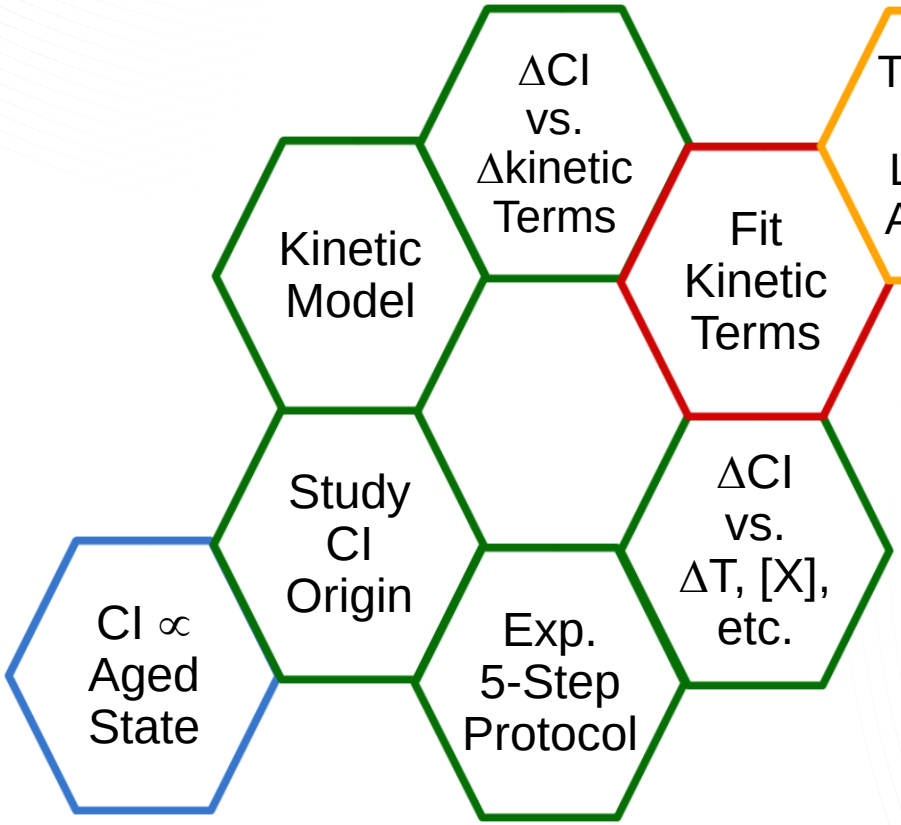
# Research Path from Observation to Improved Fuel Economy




How kinetic pathways vary

- Catalyst age
- Reaction conditions
- Catalyst formulation



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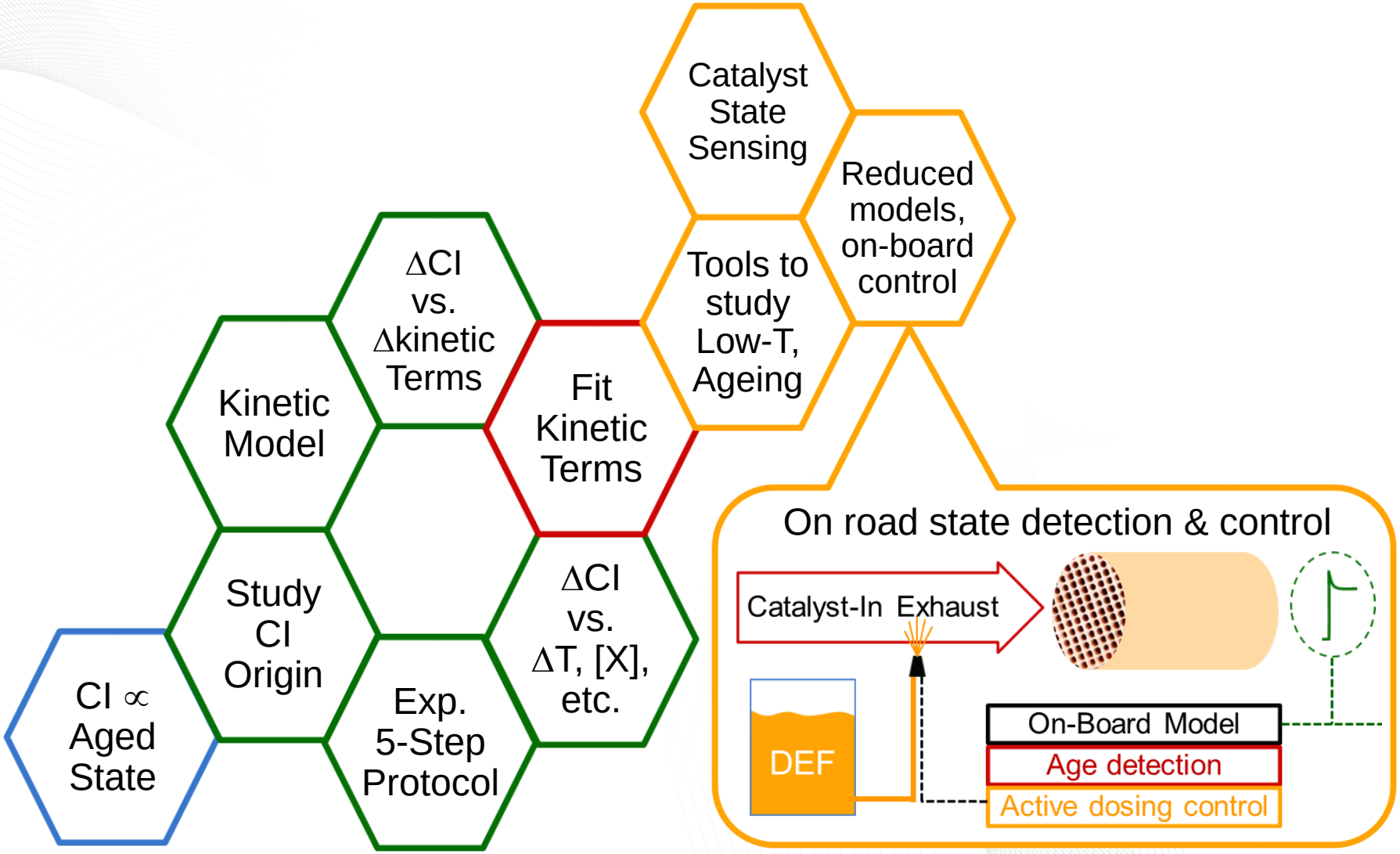
# Research Path from Observation to Improved Fuel Economy



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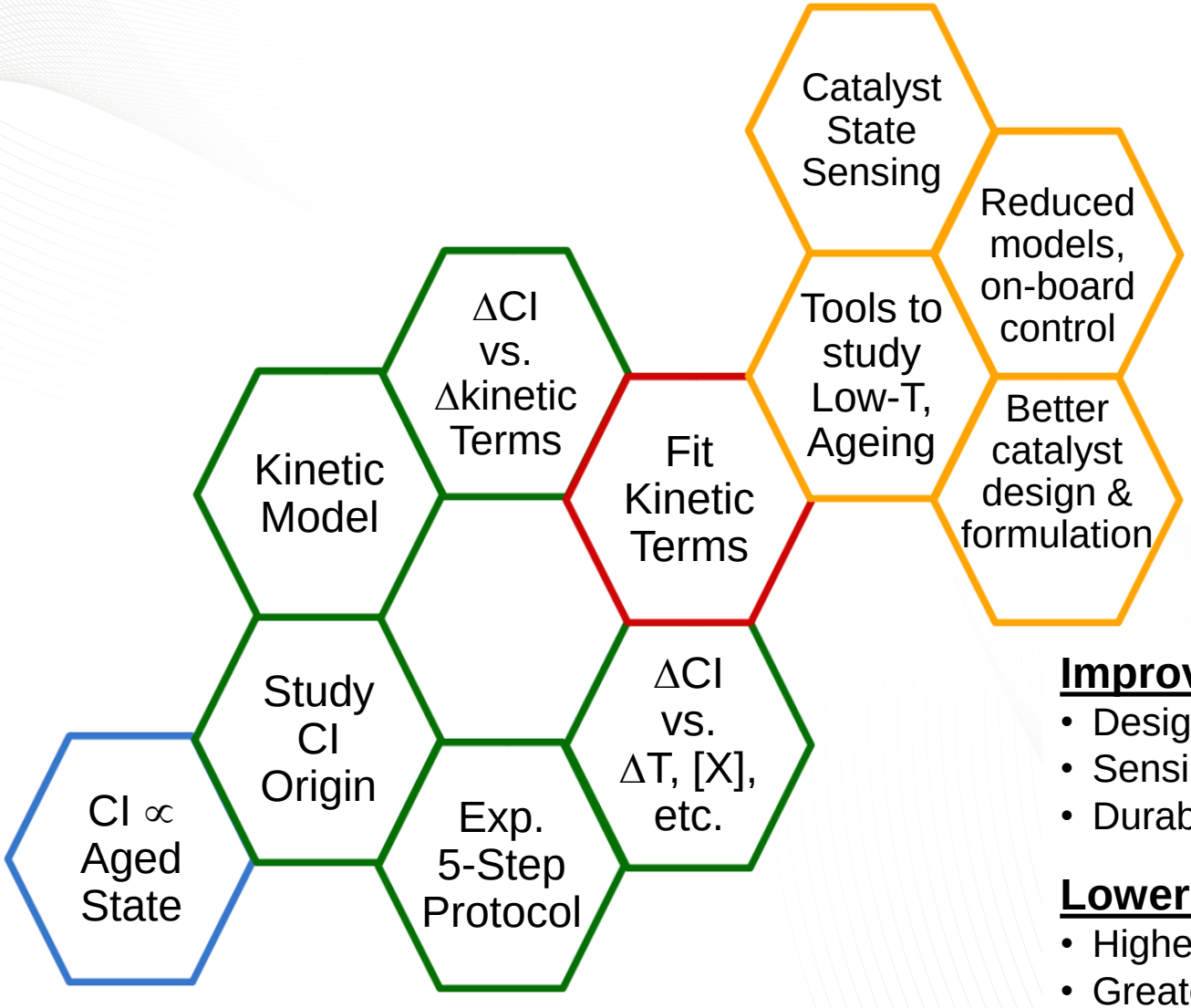
# Research Path from Observation to Improved Fuel Economy




**Improved aftertreatment:**

- Design & cost
- Sensing & control
- Durability

**Lower engine margins:**

- Higher engine-out emissions
- Greater fuel economy
- Better engine durability



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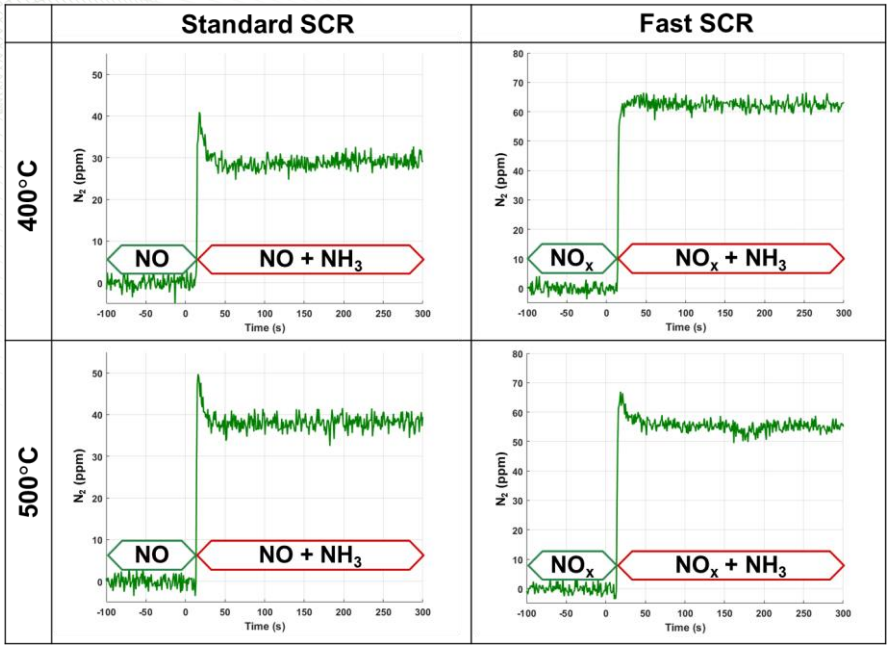
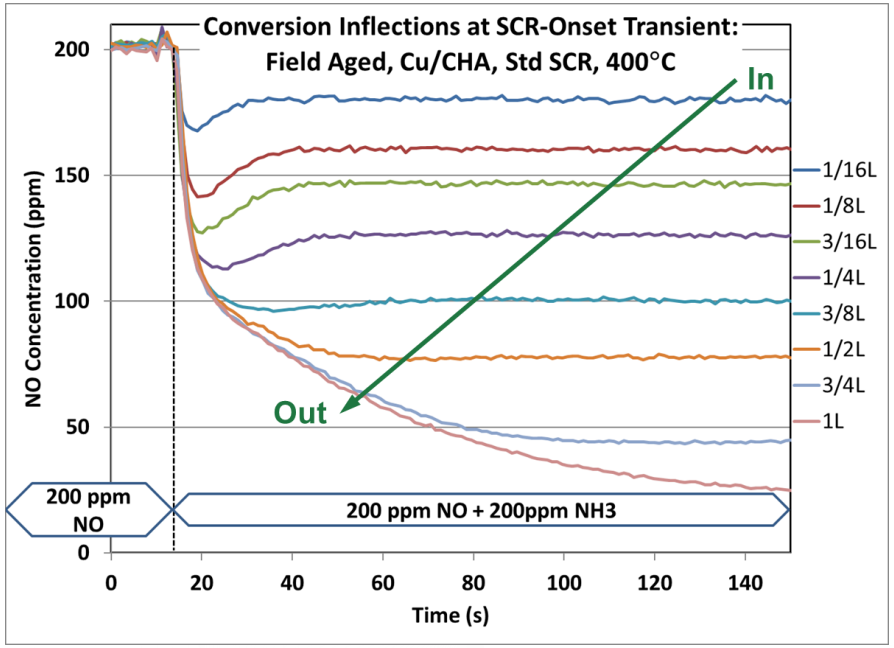
# SCR-Onset Conversion Inflections Vary with Conditions




- CI nature varies with SCR type, temperature & along catalyst axis
  - More apparent for Standard SCR, at higher temperatures, and at catalyst front
  - Only apparent with Fast SCR at higher temperatures

***Study CI to understand its origins***

***Apply CI to improve SCR knowledge & predictive models***



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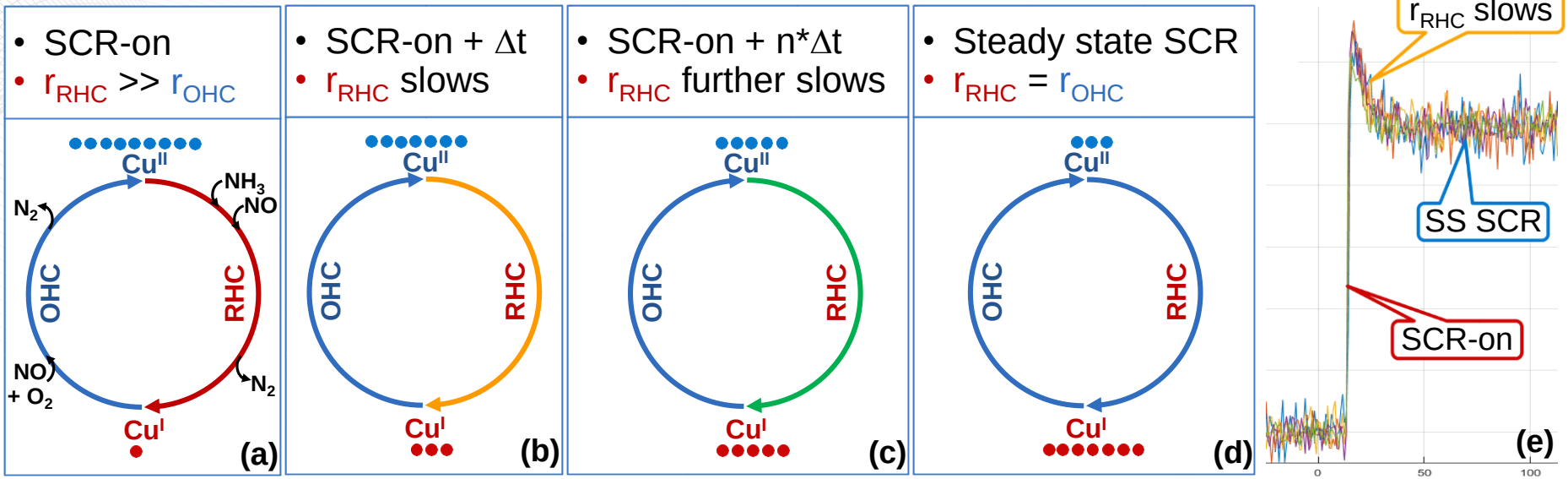
# Conceptual Model of Cu/SCR CI Origin




- Cu SCR can be viewed as cyclic Cu reduction and oxidation
  - **RHC: Reduction Half Cycle** – oxidized Cu ($Cu^{II}$) is reduced to $Cu^{I}$
  - **OHC: Oxidation Half Cycle** – $Cu^{I}$ is reoxidized to $Cu^{II}$ completing the cycle
- Half-cycle rate imbalances induce CI at SCR onset
  - CI occurs when the RHC rate is faster than the OHC rate; $r_{RHC} > r_{OHC}$
  - $r_{RHC}$ progressively slows to match $r_{OHC}$ at steady state
- Half-cycle kinetic model was formulated & exercised to investigate CI nature



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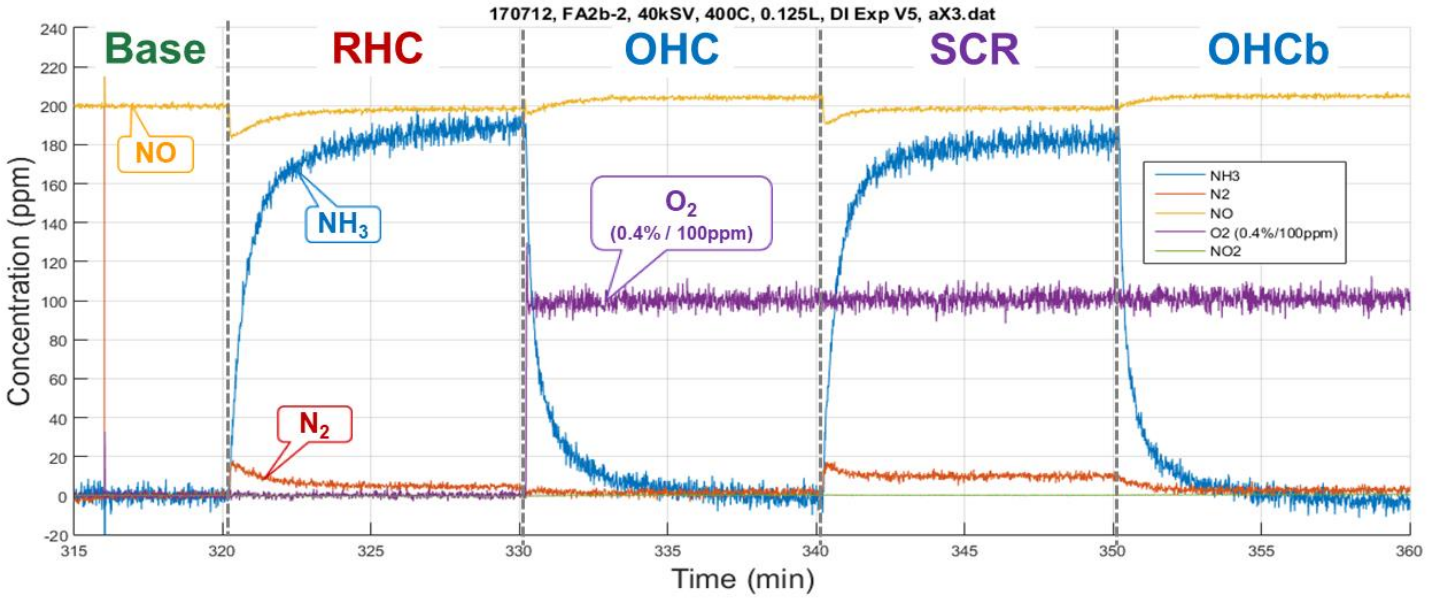
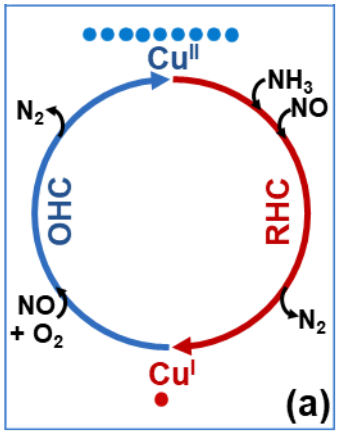
# Measuring Individual & Combined Half-Cycle Transients




- Experimental 5-Step protocol probes SCR half-cycle components
- Individual RHC, OHC & SCR transitions investigated
  - Step 1 - Base: 5% $H_2O$ + 200ppm $NO_x$ in Ar
  - Step 2 - RHC: Base + 200ppm $NH_3$
  - Step 3 - OHC: Base + 0.4% $O_2$
  - Step 4 - SCR: Base + 0.4% $O_2$ + 200ppm $NH_3$
  - Step 5 - OHCb: Base + 0.4% $O_2$

**Transient nature reflects the half-cycle kinetic parameters**

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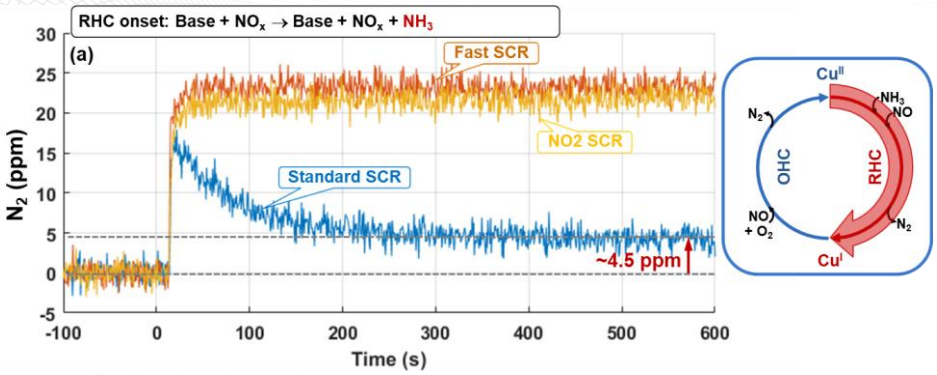
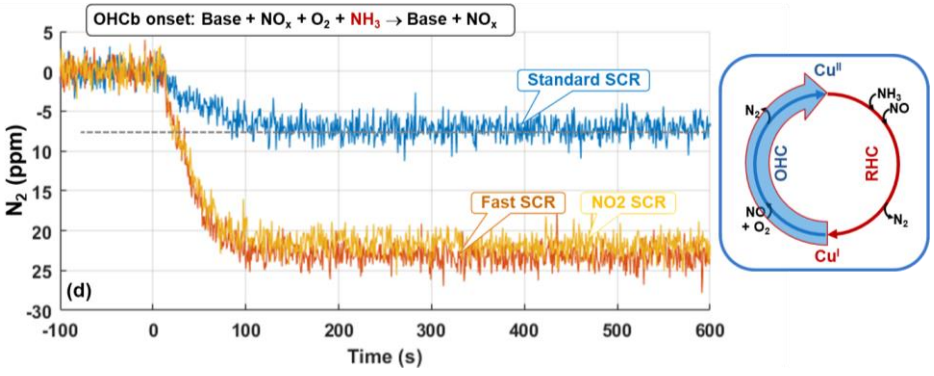
# Transient Response Probes Differences in Half-Cycle Kinetic Parameters and Reaction Pathways




- Transient response differs for RHC & OHC half-cycles
  - Reflects half-cycle-specific kinetics
- Transients differ with SCR type (Standard, $NO_2$, Fast)
  - Reflects different reaction pathways
- SCR shows additional variations (see Tech. Backup Slides)
  - Reflects combined impact of simultaneous RHC & OHC

**Use transient measurements to quantify RHC & OHC kinetic parameters**



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# SCR Models Formulated Based on RHC & OHC Half-Cycles

**Standard SCR**

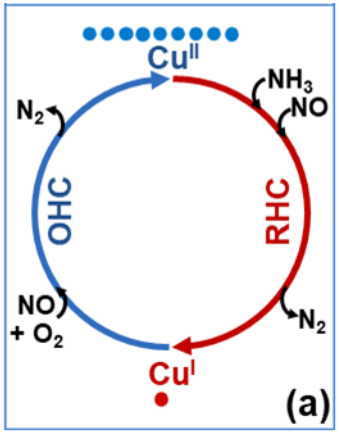
RHC: $Cu^{II}(OH)(NH_3) + 2{\cdot}NH_3 + NO \rightarrow Cu^{I}(NH_3)_2 + N_2 + 2H_2O$

$r_{RHC} = k_{RHC} \cdot [Cu^{II}] \cdot [NO] \cdot (\theta_{NH3})^{\sim 0} \cong k_{RHC} \cdot [Cu^{II}] \cdot [NO]$

OHC: $2{\cdot}Cu^{I}(NH_3)_2 + O_2 + 2{\cdot}NO \rightarrow 2{\cdot}\ Cu^{II}(OH)(NH_3) + 2{\cdot}N_2 + 2{\cdot}H_2O$

$r_{OHC} = k_{OHC} \cdot [Cu^{I}]^2 \cdot [O_2] \cdot [NO]$

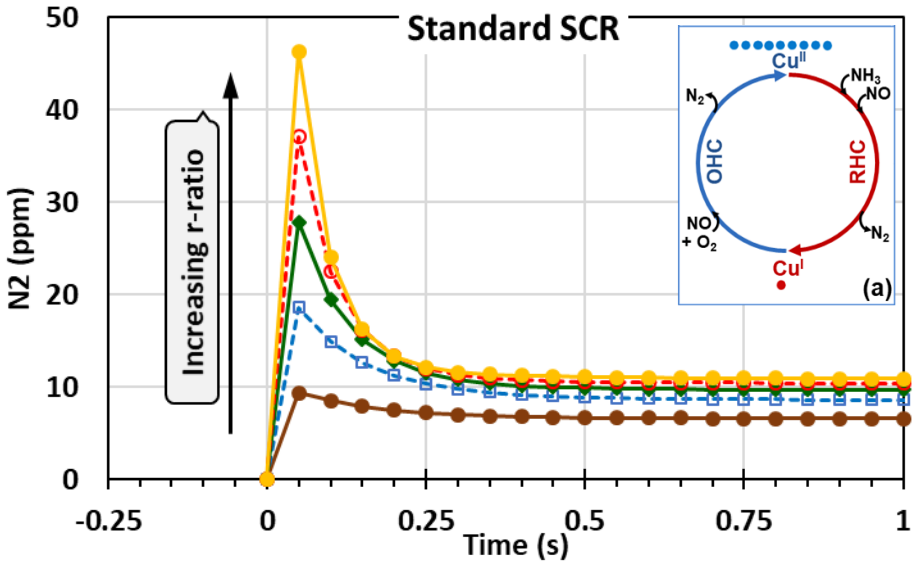
Net Standard SCR: $4{\cdot}NO + 4{\cdot}NH_3 + O_2 \rightarrow 4{\cdot}N_2 + 6{\cdot}H_2O$

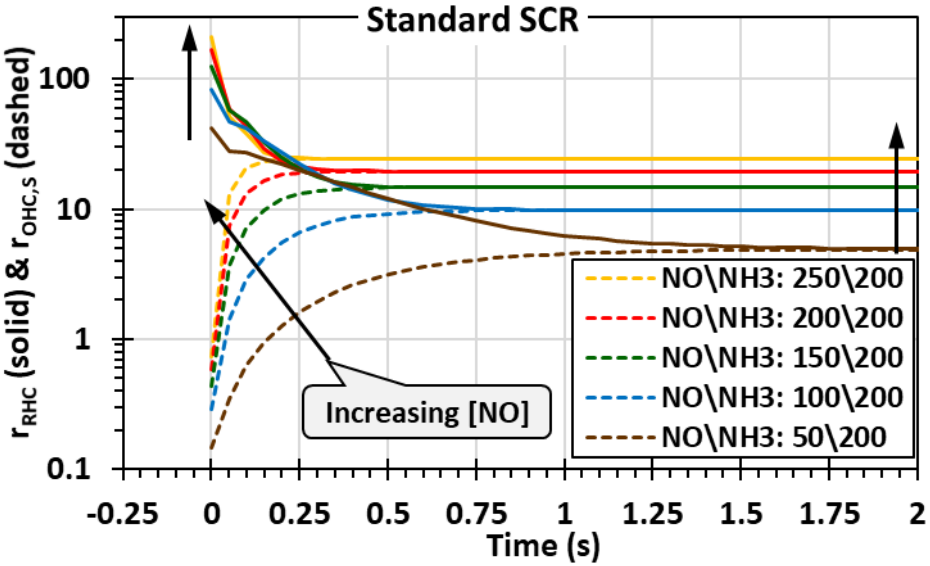



- Half-cycle models formulated for Standard & Fast SCR (see Tech. Backup Slides)
  - Many different ways to formulate
  - Half-cycle kinetic parameters to be determined
  - Correct combination will accurately predict onset-transient response

- Exercise model to study transient CI nature
  - Origin
  - Variation with model formulation & kinetic parameters
  - Consistency with experimental trends

# Model Predicts Systematic CI Transient Variations




- CI becomes more distinct with increasing half-cycle rate imbalance
  - r-ratio = $r_{RHC}$ / $r_{OHC}$
- Half-cycle rates converge faster with increasing [NO]
  - Rate convergence is consistent with conceptual model
- Many trends useful for guiding predictive-model development
  - CI increases with temperature
  - Stoichiometry transient reflects varying dominance & balancing of half cycles

**CI nature varies in consistent way with half-cycle kinetic parameters**



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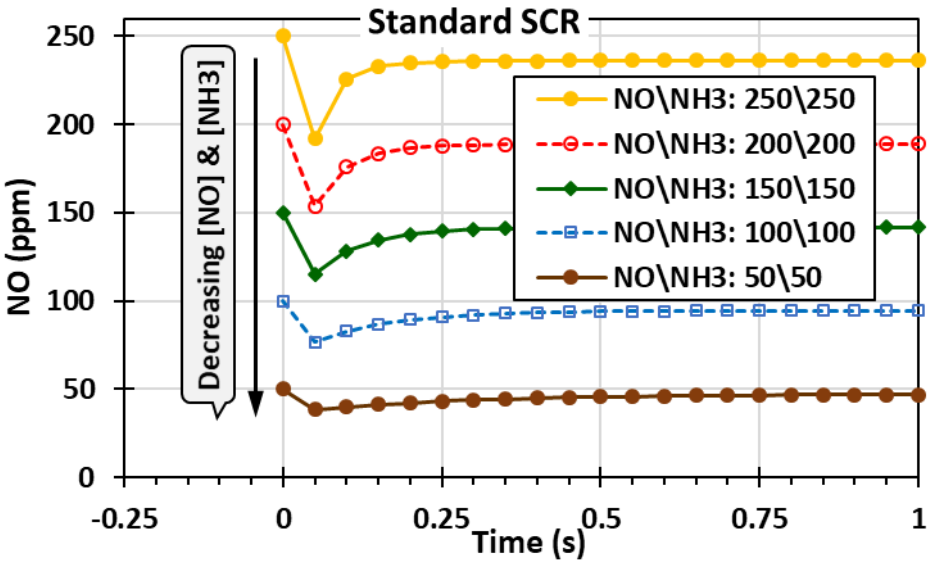
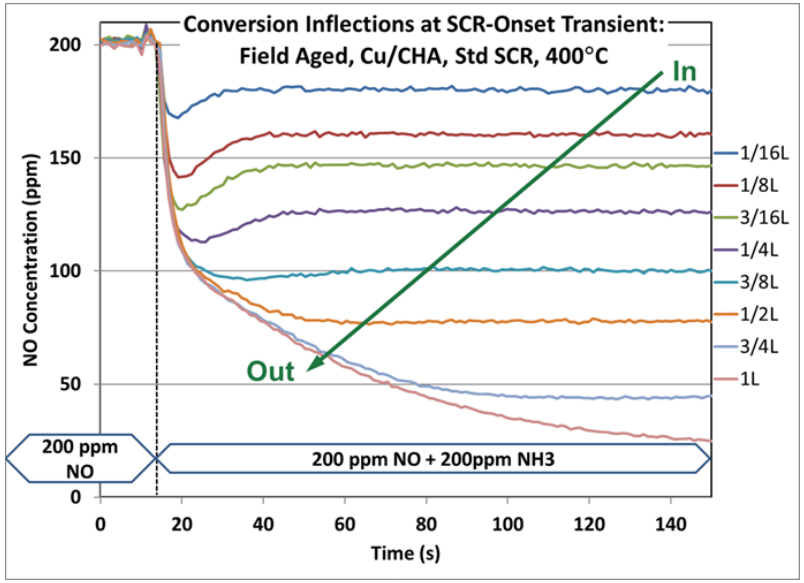
# Model Trends are Consistent with Measurement Trends




- Predicted NO CI trends are consistent with spatiotemporal measurements
  - Greatest CI at catalyst front
  - CI degrades along catalyst as NO-conversion progresses
- Predicted CI temperature trends also consistent with measurements

- **Consistent trends suggest CI is due to half-cycle rate imbalances**
- **Proposed Cu-redox model appropriate for describing SCR transients**
- **Suggests joint model-measurement study to determine SCR kinetic parameters**

# Remaining Challenges & Future Work

## Key Challenge:

- Efficient catalyst performance under aged & low-temperature operating conditions
  - How does ageing impact SCR reaction network
  - Mechanistic impact of 'low-temperature' SCR formulations

## Future Work:

- Protocol experiments to characterize transient nature
  - Temperature, composition & stoichiometry dependence
- Determine RHC & OHC kinetic parameters
  - Formulate & tune SCR redox model using measurements
- Analyze how parameters are impacted by ageing and composition
  - Analyze various catalyst samples: baseline, aged, composition
  - Sensitivity of each half cycle, and parameter
- Use insights to advance catalyst technology
  - Improved predictive models for design & on-road control
  - Methods for catalyst-state sensing
  - Improving catalyst formulation

Any proposed future work is subject to change based on funding levels

# Collaborations & Coordination

- **Cummins**
  - Project Partner, Saurabh Joshi (Co-PI)

**Teamwork & Roles**

| Cummins | Joint | ORNL |
|---|---|---|
| • Catalyst samples | • Planning | • Diagnostics |
| • Field & other ageing | • Results interpretation | • Measurements |
| • Detailed modeling | • Monthly+ telecoms | • Data analysis |

- **Technical update to Advanced Engine Crosscut**
  - May 10, 2018

- **Interactions with technical community**
  - 1 archival publication

    W.P. Partridge, S.Y Joshi, J.A. Pihl, N.W. Currier (2018). "New Operando Method for Quantifying the Relative Half-Cycle Rates of the NO SCR Redox Cycle Over Cu-Exchanged Zeolites," Applied Catalysis B: Environmental. doi.org/10.1016/j.apcatb.2018.04.071 ; Available online 1 May 2018

  - 2 invited book chapters
  - 4 presentations (2 invited)

# Responses to 2017 Review Comments

## Recommendations:

- A more demonstrated understanding of differences between CI predictions and measurements is needed
- Show how CI phenomenon can be modeled and related to OBD or dosing strategy
  - ***CI model has been focus this year, and shown in AMR presentation and publication***
  - ***These results explain the differences noted in the '17AMR presentation, and provide a consistent CI understanding between measurements and model***
  - ***Follow-on work will focus on detailed model based on the Cu half cycles***
  - ***Out-year research will focus on applications for state assessment and control***
    - ***basic evidence and concepts for this have been shown in previous presentations***

- Give more detail
  - ***More detail has been provided this year in Tech. Backup Slides***
  - ***Publication will provide more detail than is possible in presentation***

- Study range of SV
  - ***Spatially resolved measurements cover a range of effective SV***
  - ***E.g., 1/8, 1/4 & 1/2L locations have 8x, 4x & 2x, respectively, SV of the 1L location***
  - ***SV can be swept in future detailed model for comparison to these measurements***

- Cummins interest is unclear, & suggest partner to focus on extracting non-proprietary content for general use
  - ***CMI did all the detailed modeling presented last year***
  - ***CMI & ORNL jointly develop and implement the research plan***
  - ***The half-cycle kinetic model is completely open and has been published***
  - ***The project has an excellent record of extensively sharing results with the VT community***
  - ***The project did share performance measures of the CMI corporate SCR model relevant to the CI study; this has value beyond the CI application and those requiring access to the model details***

# Summary

- **Relevance**
  - Project work enables improved catalyst knowledge, models, design, OBD & control
  - This reduces catalyst system costs & required engine-efficiency tradeoffs
  - This in turn enables DOE goals for improved fuel economy
- **Approach**
  - Develop & apply diagnostics to characterize catalyst nature
  - Analyze data to understand details of catalyst functions, interrelations & ageing impacts
  - Develop catalyst-state-assessment methods & predictive catalyst models
- **Technical Accomplishments**
  - Experimental method for studying half-cycle origin of CI developed and implemented
  - Half-cycle Cu-redox SCR model developed and exercised to study CI nature
    - Dependence on various kinetic parameters and reaction conditions shown
  - Step-Response method demonstrated for formulating, tuning and validating SCR models
    - Applicable for catalyst-state assessment & enabling more robust predictive model
- **Collaborations**
  - Communicate results with Crosscut team & community via presentations & publications
  - Coordination & collaboration with other DOE projects to maximize benefit
- **Future Work** (Any proposed future work is subject to change based on funding levels)
  - Develop SCR model with improved transient response based on RHC & OHC half cycles
  - Apply new Protocol and Mode to gain insights into SCR ageing mechanisms

# ***Technical Back-Up Slides***

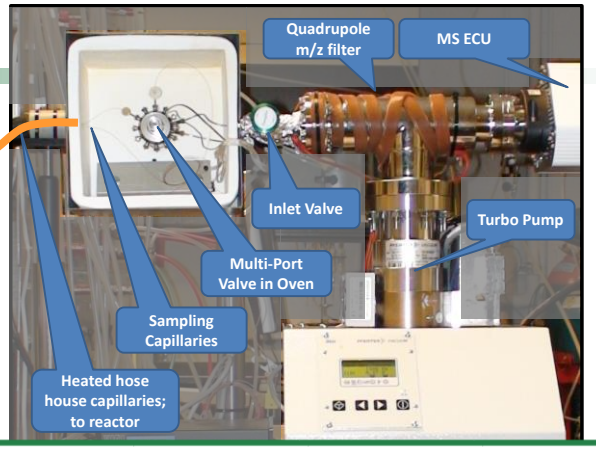
# Project Approach

## Catalyst Samples

- Commercial Cu/CHA
- Cummins brings supplier knowledge
- Representative field-aged samples
  - Typical of 100s of field-use samples

## FTIR

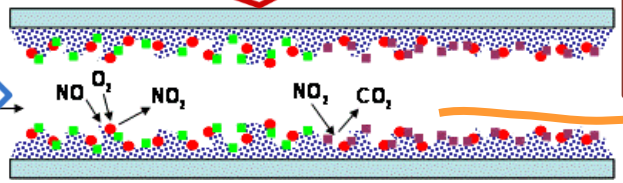
- Effluent species

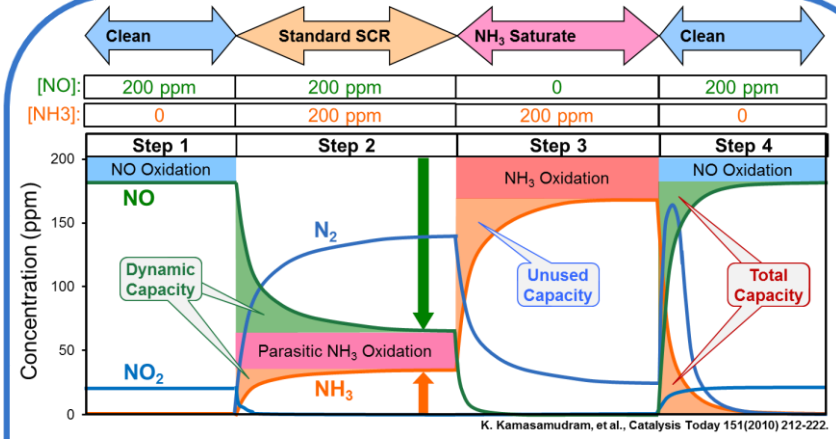



## SpaciMS

- Spatial & temporal mapping
- NO, $NH_3$, $N_2$, $NO_2$, $N_2O$, other
- $^1/_{16}$, $^1/_8$, $^1/_4$, $^1/_2$, $^3/_4$, 1L…locations

Gas Mix In




## 4-Step & Other Protocols

- Different T & species combinations
- Steady state & transient analysis
- Probes specific reactions & functions

## Predictive Catalyst Models

- Cummins brings extra-project knowledge
- Project focuses on data for critical assessment & insights for improvement

## Enabling Project Contributions

- Functional relationships & ageing impacts
  - Insights for improved modeling & state sensing
- Catalyst-state sensing
  - Sensing, OBD, efficiency, durability
- Robust & accurate predictive models
  - Design, efficiency, control, durability



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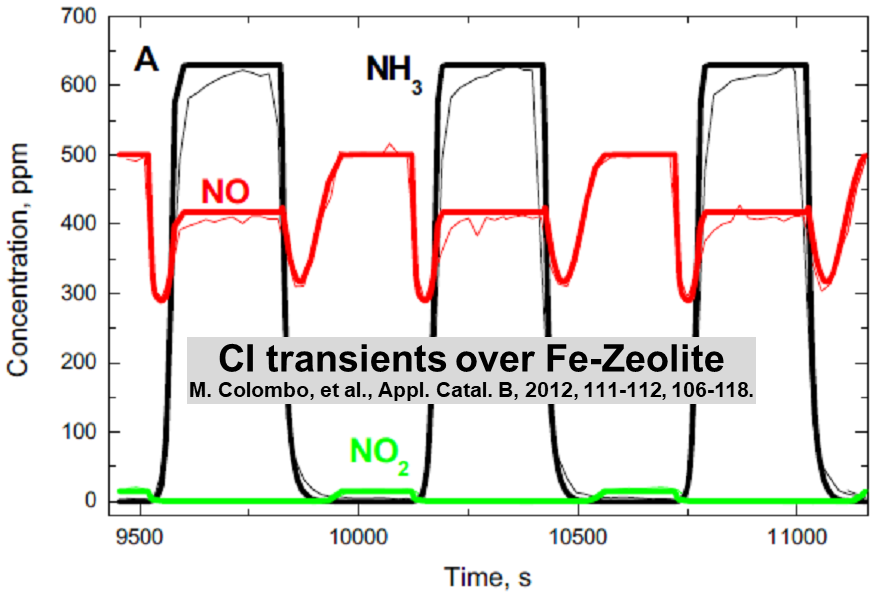
# $NH_3$-Coverage Inhibition Dynamics with Fe/SCR Catalysts




- Dynamic $NH_3$–coverage inhibition can induce CI in Fe/SCR catalysts
  - Observe at both SCR onset and termination
  - More apparent at higher coverage; i.e., lower temperatures
- Cu/SCR CI does not follow these trends
  - Only apparent at SCR onset and not at termination
  - More apparent at higher temperatures where $NH_3$ coverage is lower
- Origin of Cu/SCR CI is different from that of Fe/SCR CI
  - Cu/SCR CI is apparently not due to $NH_3$-coverage inhibition



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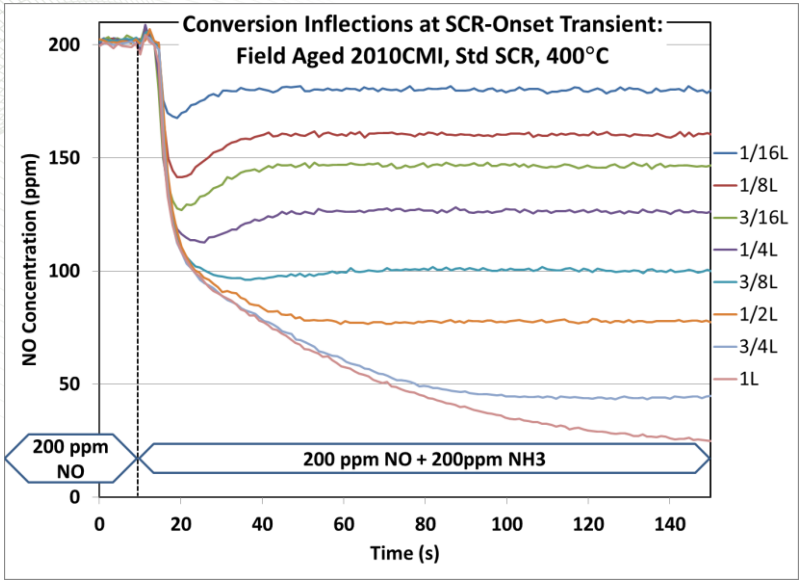
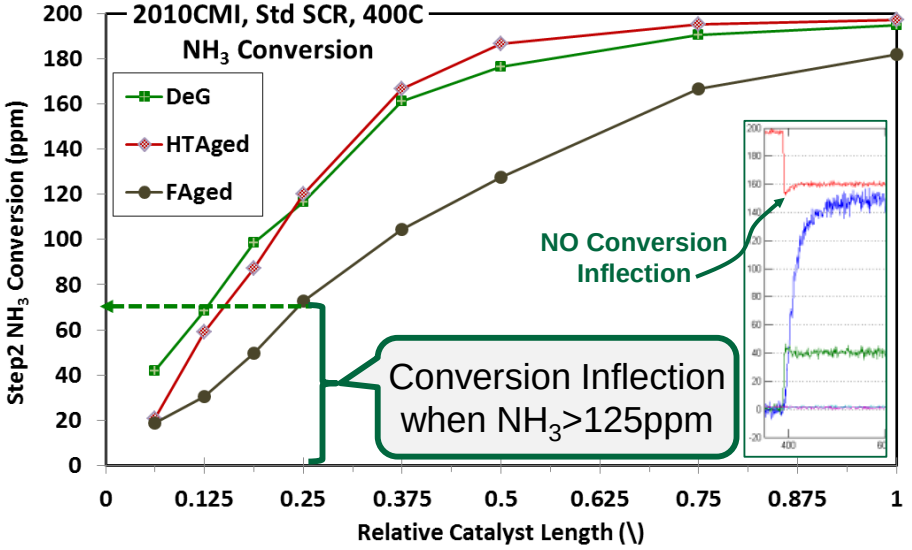
# Conversion Inflections may provide Measure of Catalyst State




Partridge, et al., 2015 CLEERS Workshop

- CI transients vary systematically with conditions and catalyst state
  - Exist deeper into catalyst with lower conversion; due to T, composition, age, etc.
  - Observed above a consistent temperature-dependent $NH_3$ threshold
- Relevant to catalyst-state assessment, control & OBD
  - E.g., correlate CI timing or location with aged state
  - Feedback for adjusting urea dosing, or model-based control parameters



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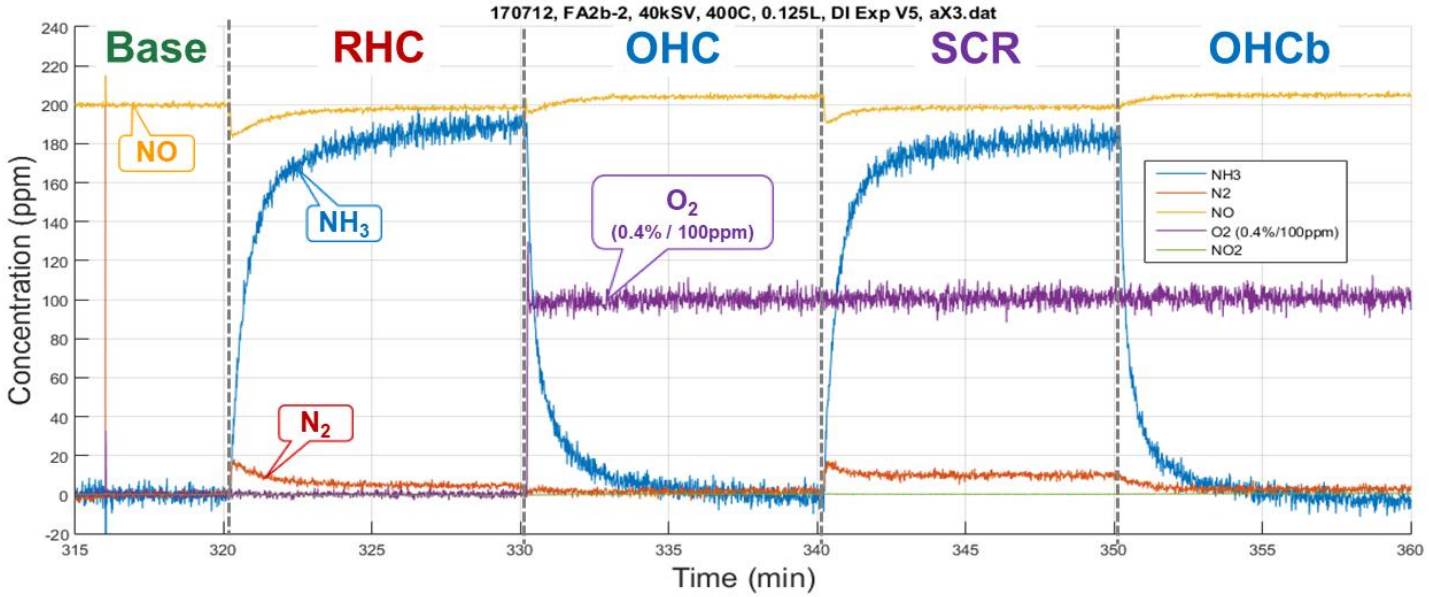
# 5-Step Experimental Protocol for Studying Onset Transients




- Individual RHC, OHC & SCR transitions investigated
  - Step 1 - Base: 5% $H_2O$ + 200ppm $NO_x$ in Ar
  - Step 2 - RHC: Base + 200ppm $NH_3$
  - Step 3 - OHC: Base + 0.4% $O_2$
  - Step 4 - SCR: Base + $O_2$ + 200ppm $NH_3$
  - Step 5 - OHCb: Base + $O_2$
- Different SCR mixtures investigated
  - Standard, Fast & $NO_2$
  - 200ppm $NO_x$

- Commercial CHA SCR
- Field Aged: FA-2b
- 400°C
- 1/8L
- 40k SV

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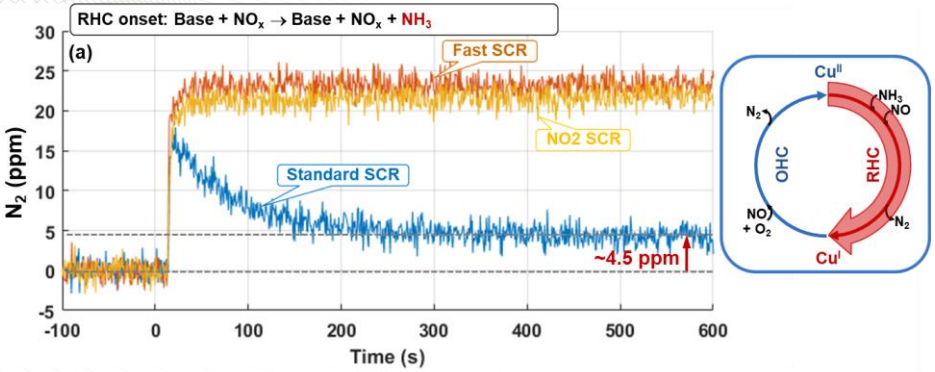
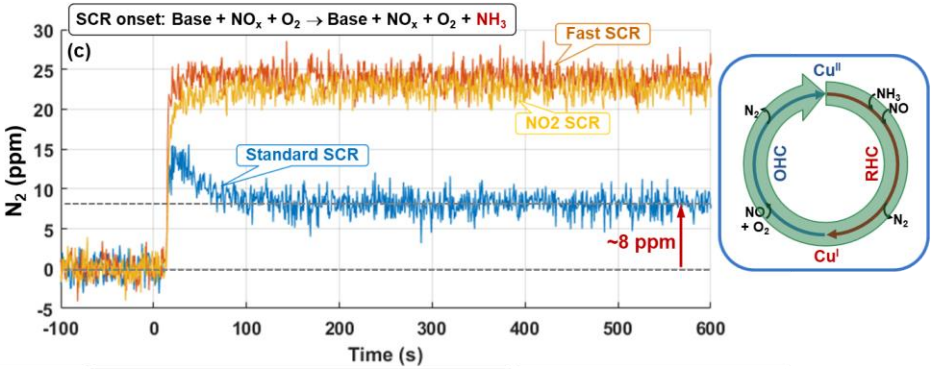
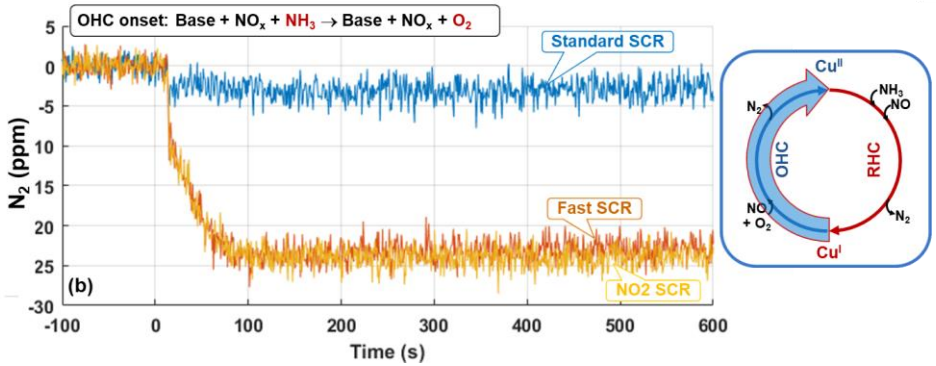
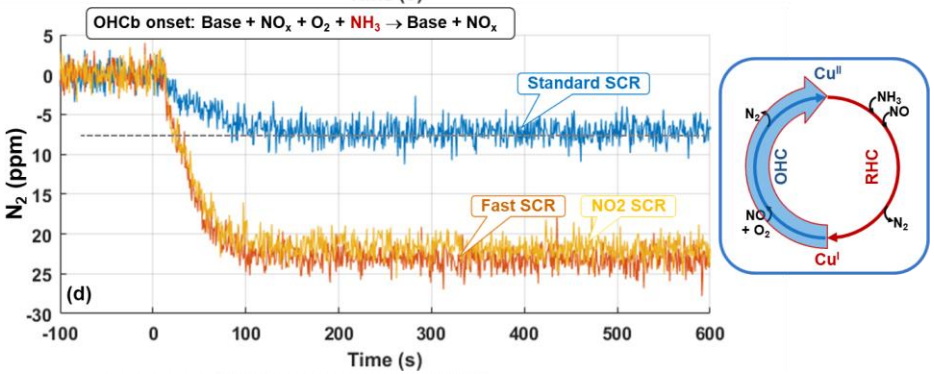
# Measured Half-Cycle Onset Transients



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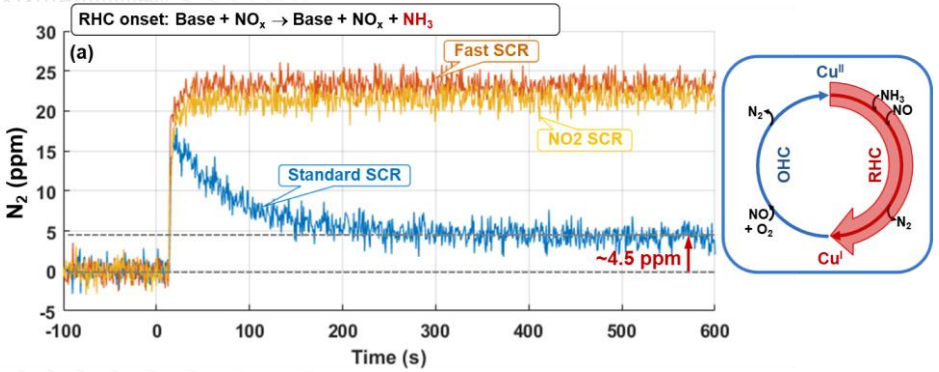
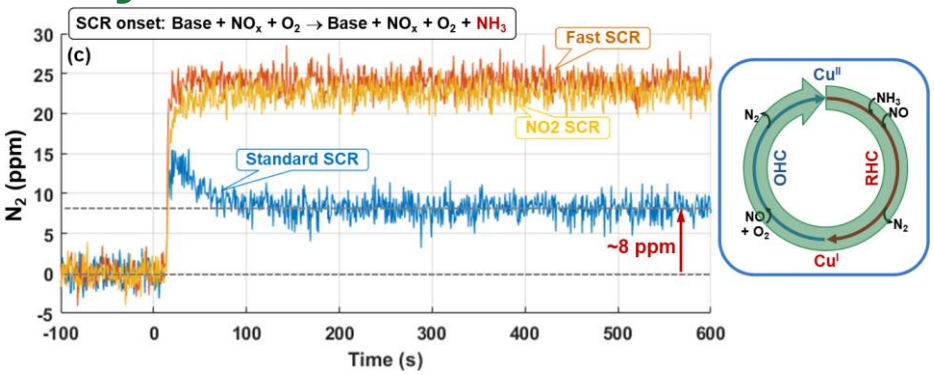
# Measurements of Individual Half-Cycle Onset Transients




- 5-Step Experimental Protocol designed to study half-cycle onset transients & CI
  - Allows individual and combined half cycles to be probed (see Tech. Backup Slides)
- Standard SCR Onset Transients
  - RHC onset shows CI
    - Initial fast step-like transients indicates native RHC rate
    - Conversion degrades over ~200s as $Cu^{II}$ is depleted
    - Non-zero SS due to contaminant or bulk oxygen driving OHC
  - For SCR onset
    - CI is smaller & faster, and SS conversion is greater
    - both half-cycles are active
- $NO_2$ & Fast SCR Onset Transients
  - Identical, fast, step-like transients without CI
    - Suggests OHC occurring via $NO_2$, and $O_2$ not participating
- OHC transients offer additional insights (see Tech. Backup Slides)



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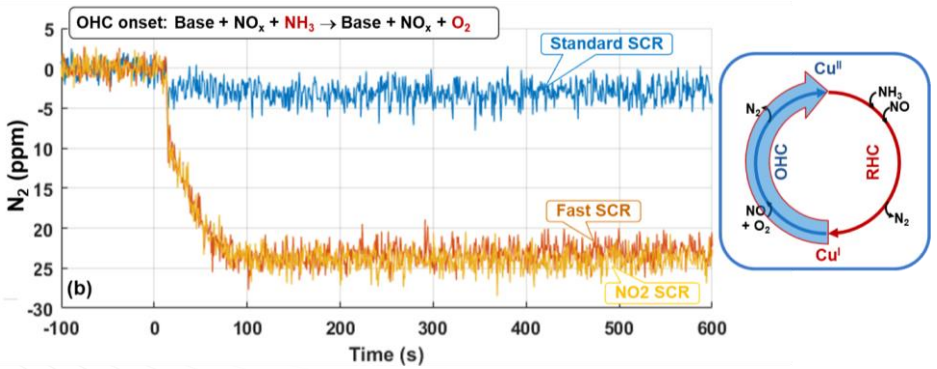
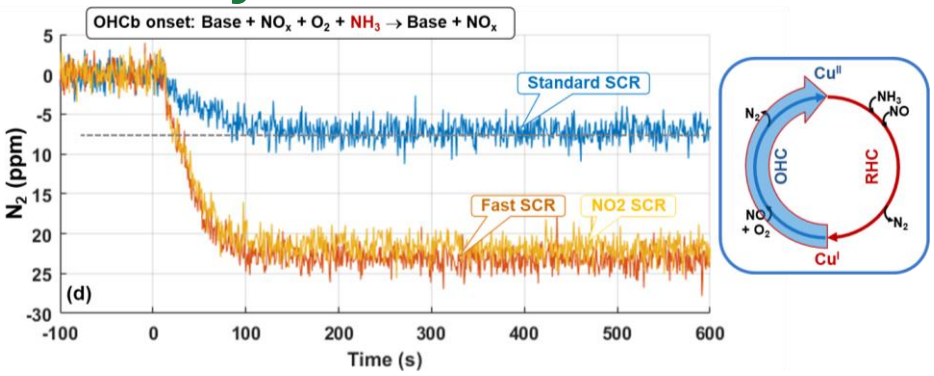
# Measurements of Individual OHC Half-Cycle Onset Transients




- OHC Onset Transients
  - Starts from maximum [$Cu^{I}$] following RHC step
    - [$Cu^{I}$] greater than at OHCb start
    - Causes greater step-like onset vs. OHCb transient
  - $NO_2$ & Fast SCR transient are identical
    - Initially step-like, then slow over ~100s as $Cu^{I}$ is depleted
  - Standard SCR show NO CI (see 5-Step Protocol figure)
    - Signal-to-noise is too small to resolve similar N2 CI
- OHCb Onset Transients
  - These follow SCR, and thus start from lower [$Cu^{I}$] initial condition
  - Slower Standard SCR transient (~150s) vs. $NO_2$ & Fast SCR (~100s)
    - Different OHC mechanism & kinetics for $O_2$- vs $NO_2$-driven OHC
  - $NO_2$ & Fast SCR transients are identical as with OHC
    - Suggests OHC driven by $NO_2$, and $O_2$ is practically inert

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# Half-Cycle based Model for Standard & Fast SCR

**Standard SCR**

RHC: $Cu^{II}(OH)(NH_3) + 2{\cdot}NH_3 + NO \rightarrow Cu^{I}(NH_3)_2 + N_2 + 2H_2O$ (1)

$r_{RHC} = k_{RHC} \cdot [Cu^{II}] \cdot [NO] \cdot (\theta_{NH3})^{\sim 0} \cong k_{RHC} \cdot [Cu^{II}] \cdot [NO]$ (2)

OHC: $2{\cdot}Cu^{I}(NH_3)_2 + O_2 + 2{\cdot}NO \rightarrow 2{\cdot}\ Cu^{II}(OH)(NH_3) + 2{\cdot}N_2 + 2{\cdot}H_2O$ (3)

$r_{OHC} = k_{OHC} \cdot [Cu^{I}]^2 \cdot [O_2] \cdot [NO]$ (4)

Net Standard SCR: $4{\cdot}NO + 4{\cdot}NH_3 + O_2 \rightarrow 4{\cdot}N_2 + 6{\cdot}H_2O$ (5)

**Fast SCR**

RHC: $Cu^{II}(OH)(NH_3) + 2{\cdot}NH_3 + NO \rightarrow Cu^{I}(NH_3)_2 + N_2 + 2H_2O$ (1)

$r_{RHC} = k_{RHC} \cdot [Cu^{II}] \cdot [NO] \cdot (\theta_{NH3})^{\sim 0} \cong k_{RHC} \cdot [Cu^{II}] \cdot [NO]$ (2)

OHC: $Cu^{I}(NH_3)_2 + NO_2 \rightarrow\ Cu^{II}(OH)(NH_3) + N_2 + H_2O$ (6)

$r_{OHC} = k_{OHC} \cdot [Cu^{I}] \cdot [NO_2]$ (7)

Net Fast SCR: $2{\cdot}NO + 2{\cdot}NO_2 + 4{\cdot}NH_3 \rightarrow 4{\cdot}N_2 + 6{\cdot}H_2O$ (8)



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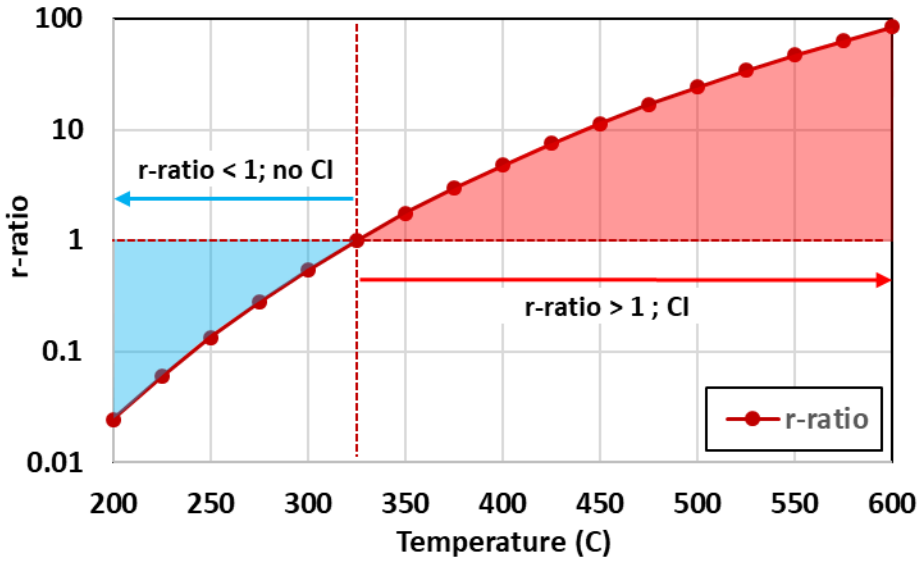
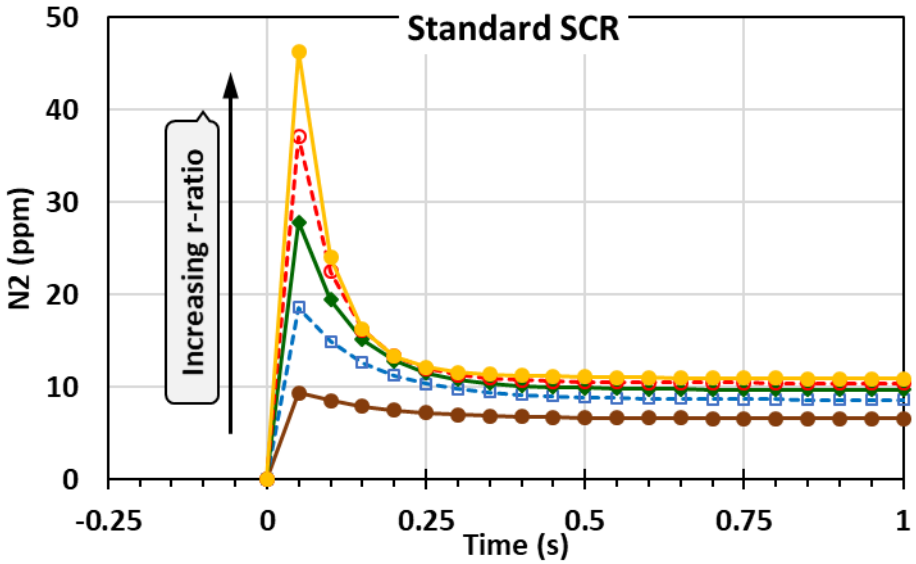
# Global Model Predicts Consistent CI Nature & Trends




- Half-cycle model exercised to study how kinetic parameters influence CI
  - Model details shown in Tech. Backup Slides
- Ratio of half-cycle rates (r-ratio = $r_{RHC}$ / $r_{OHC}$) increases with temperature
  - CI should be observed when r-ratio > unity
  - Unity crossing point tuned with RHC & OHC pre-exponential factors
- CI becomes more distinct with increasing r-ratio
  - Taller peak, faster tail
  - SS conversion increases with r-ratio
  - ***Temperature trend is consistent with experimental observations***
- ***CI nature varies with half-cycle kinetic parameters***



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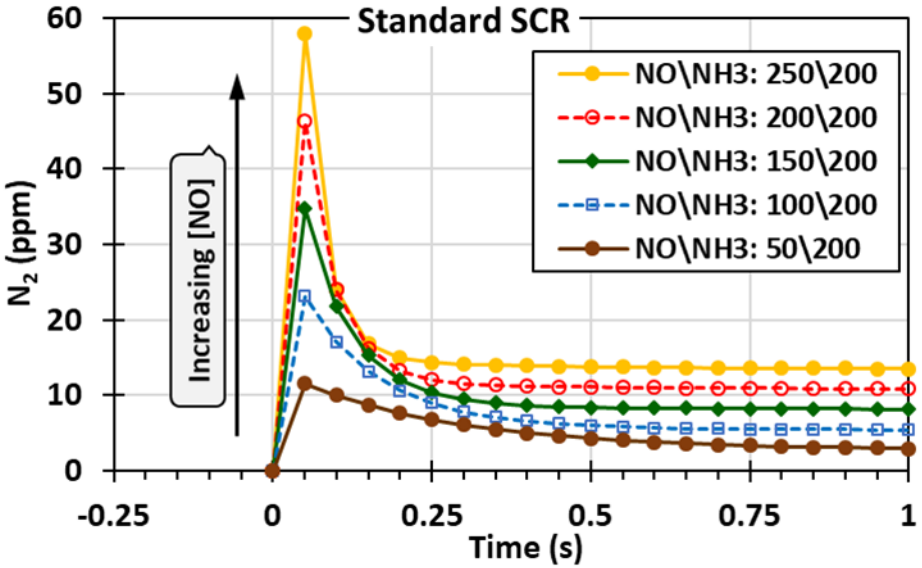
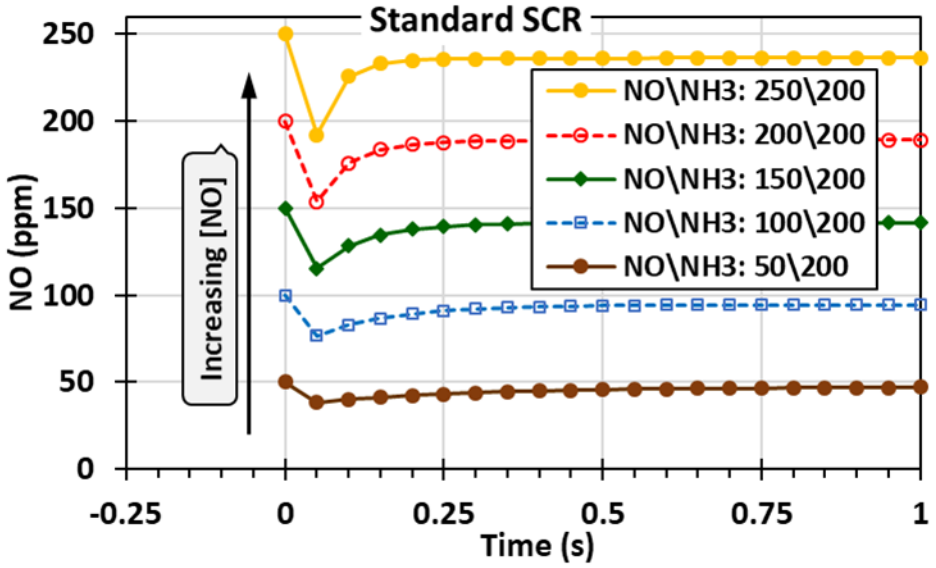
# Global Model – CI varies with NO Concentration




- Varying [NO] at constant 200ppm $NH_3$
  - CI independent of [$NH_3$], (zeroth order in [$NH_3$], see Tech. Backup Slides)
- CI becomes increasingly distinct with increasing [NO]
  - Similar for both $N_2$ & NO CI



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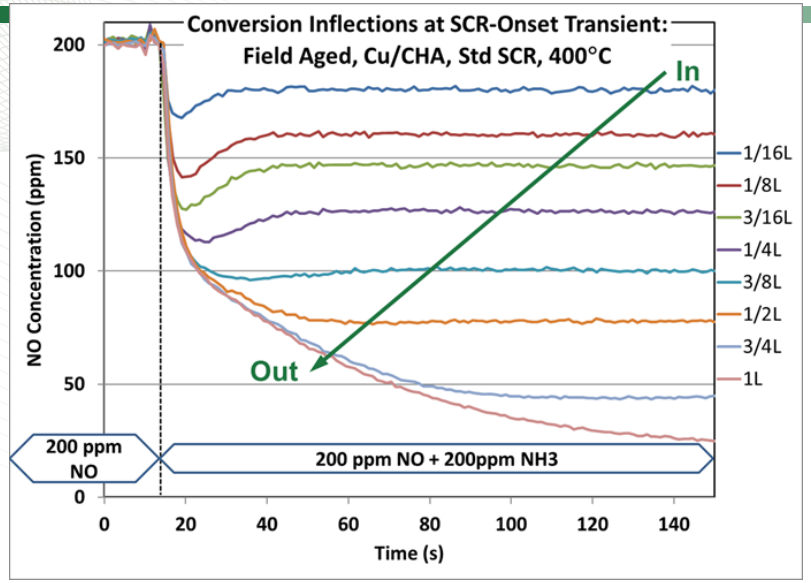
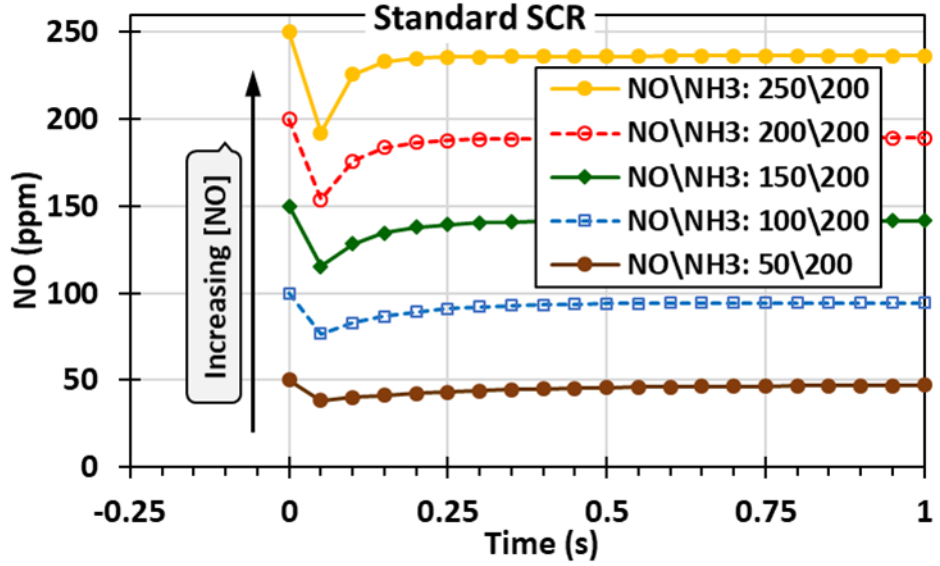
# Global Model – CI varies with NO Concentration




- Varying [NO] at constant 200ppm $NH_3$
  - CI independent of [$NH_3$], (zeroth order in [$NH_3$], see Tech. Backup Slides)
- CI becomes increasingly distinct with increasing [NO]
  - Similar for both $N_2$ & NO CI
- ***NO CI trends consistent with measured trends along catalyst axis***
  - Greatest CI at catalyst front
  - CI degrades along catalyst as NO-conversion progresses
- ***Spatiotemporal measurements may be used to tune a global model***
  - Determine half-cycle kinetic parameters from fitting model to measurement data



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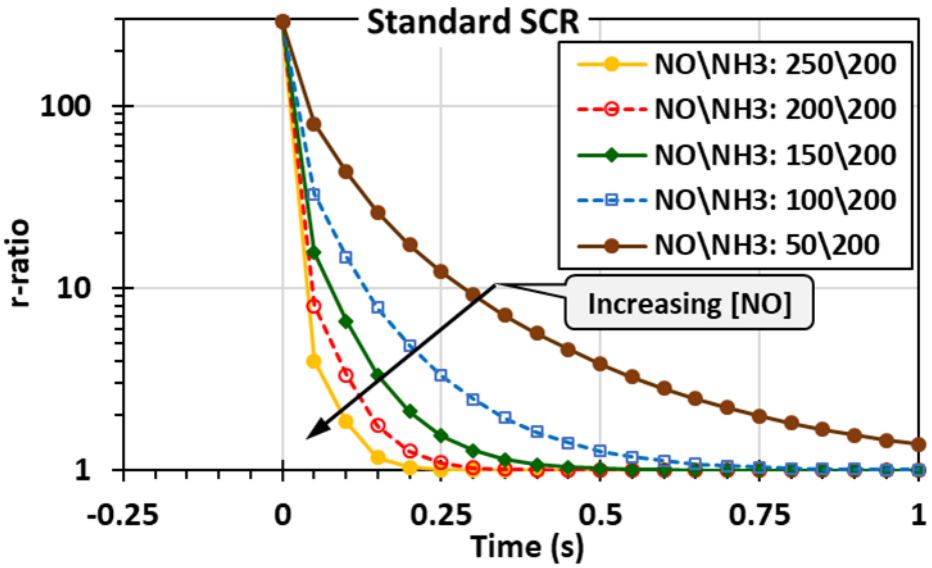
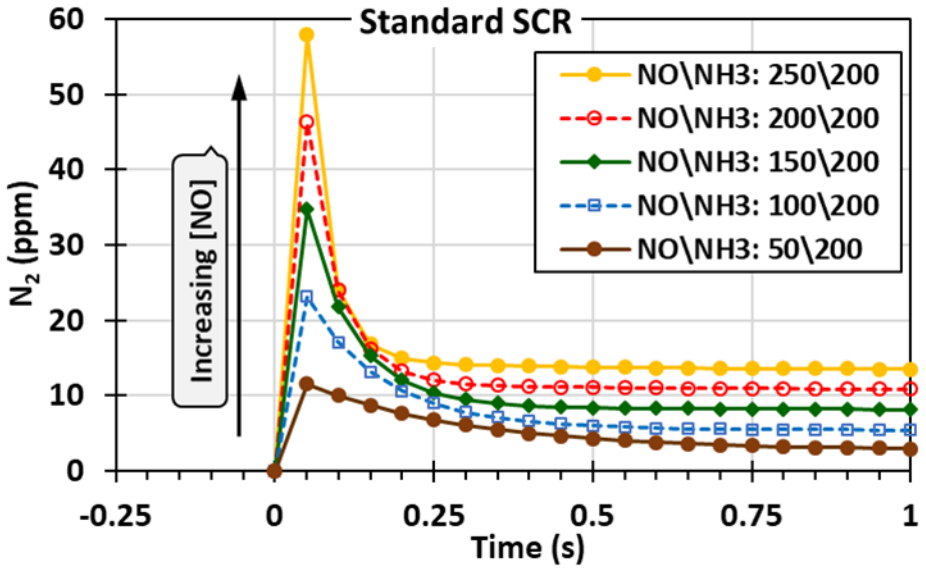
# Global Model – Half-Cycle Rates vary with NO Concentration




- r-ratio transient becomes faster with increasing [NO]
  - Distinct CI needs ***both*** r-ratio>1 ***and*** fast r-ratio transient



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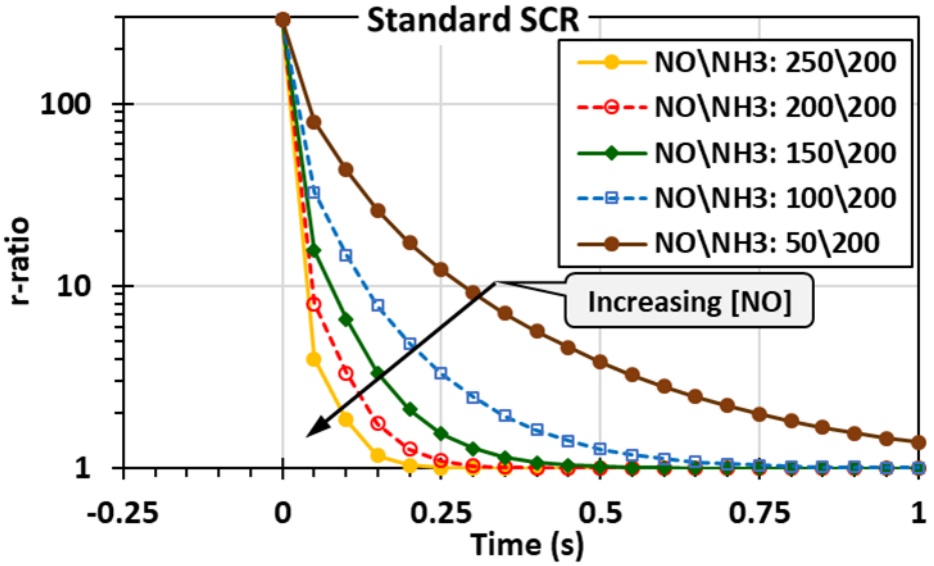
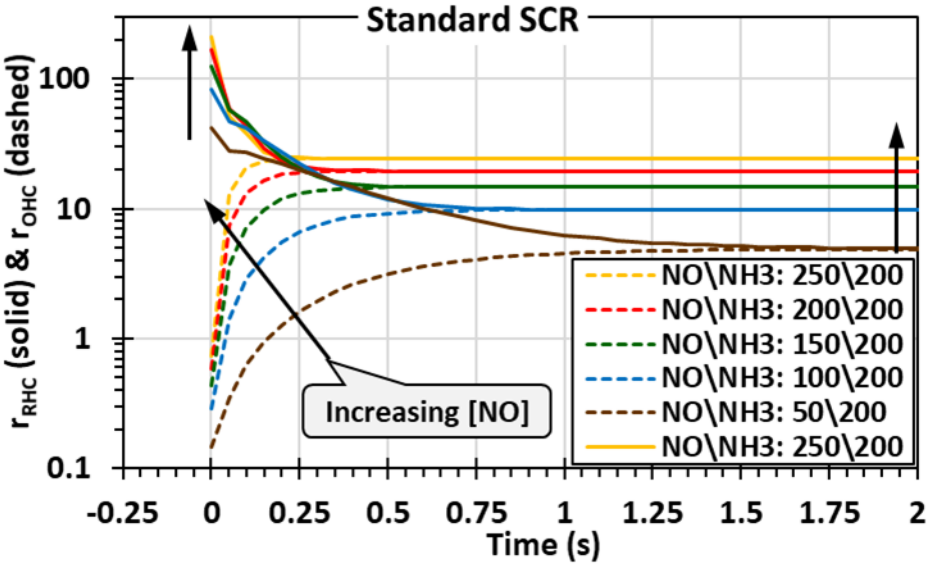
# Global Model – Half-Cycle Rates vary with NO Concentration




- r-ratio transient becomes faster with increasing [NO]
  - Distinct CI needs ***both*** r-ratio>1 ***and*** fast r-ratio transient
- RHC & OHC rates converge at steady state
  - Mainly due to RHC slowing
    - Relatively small $r_{OHC}$ increase associated with increasing $Cu^{I}$
  - Greater SS conversion & rates with increasing [NO] ***(consistent with SpaciMS)***
  - Rate transient is greater when initial difference is greater
  - ***Half-cycle rate behavior is consistent with conceptual model***
- ***Model-based studies help advance CI understanding and nature***



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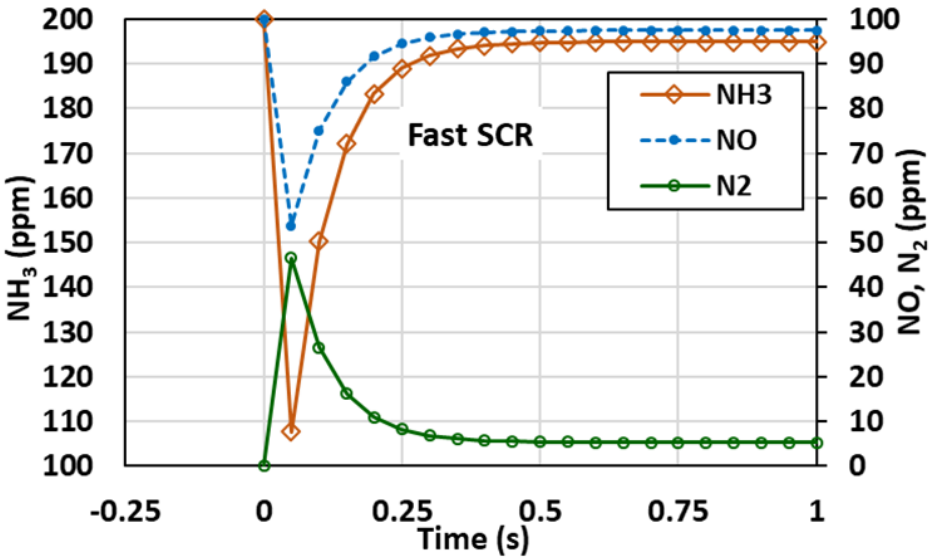
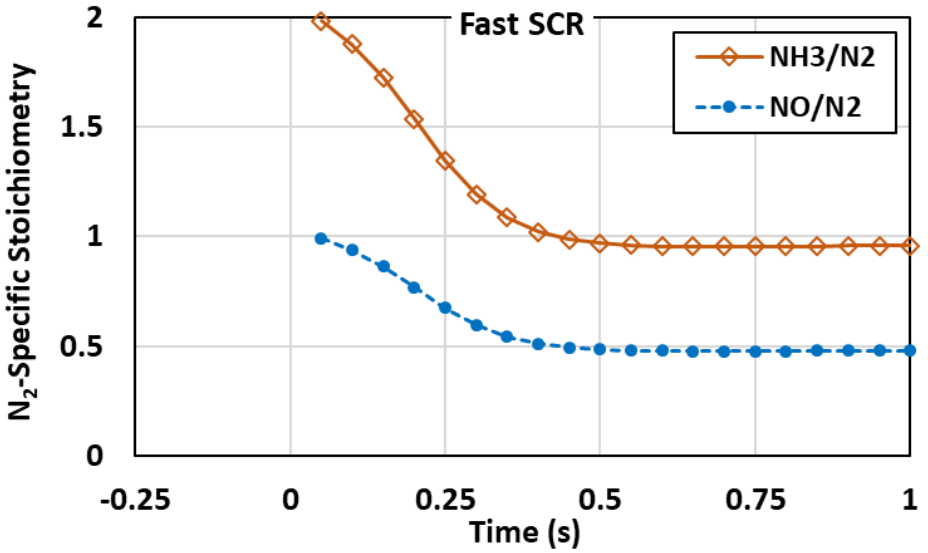
# Global Model – Stoichiometry Varies Through CI Transient




- Model predicts CI for NO, $NH_3$ and $N_2$
- CI leading edge reflects RHC stoichiometry
  - RHC: $Cu^{II}(OH)(NH_3) + 2{\cdot}NH_3 + NO \rightarrow Cu^{I}(NH_3)_2 + N_2 + 2H_2O$
- Steady state reflects Net Fast SCR stoichiometry
  - Net Fast SCR: $2{\cdot}NO + 2{\cdot}NO_2 + 4{\cdot}NH_3 \rightarrow 4{\cdot}N_2 + 6{\cdot}H_2O$
- Stoichiometry transient reflects half-cycle balancing
  - As rates converge impact of the individual half cycles balance
- Generally similar results for Standard SCR (see Tech. Backup Slides)
- ***Technique can be use to validate model formulation***



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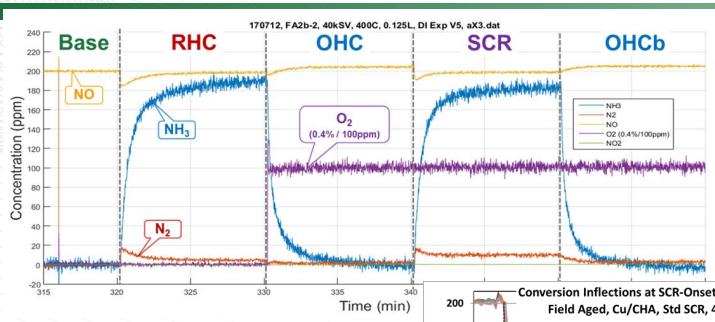
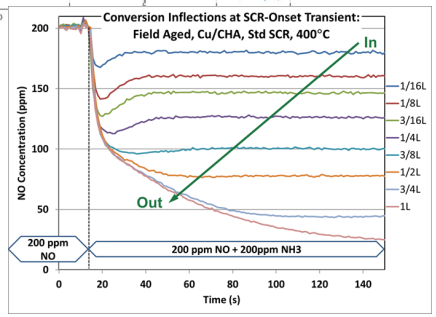
# Methodology for Formulating & Validating SCR Redox Model



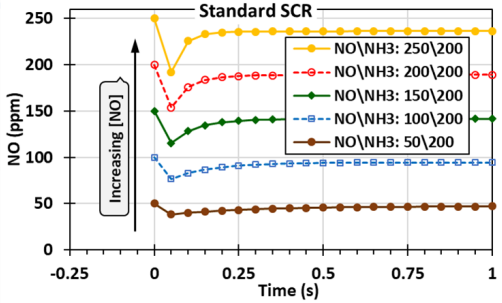

RHC: $Cu^{II}(OH)(NH_3) + 2{\cdot}NH_3 + NO \rightarrow Cu^{I}(NH_3)_2 + N_2 + 2H_2O$

$r_{RHC} = k_{RHC} \cdot [Cu^{II}] \cdot [NO] \cdot (\theta_{NH3})^{\sim 0} \cong k_{RHC} \cdot [Cu^{II}] \cdot [NO]$

OHC: $2{\cdot}Cu^{I}(NH_3)_2 + O_2 + 2{\cdot}NO \rightarrow 2{\cdot}\ Cu^{II}(OH)(NH_3) + 2{\cdot}N_2 + 2{\cdot}H_2O$

$r_{OHC} = k_{OHC} \cdot [Cu^{I}]^2 \cdot [O_2] \cdot [NO]$

Net Standard SCR: $4{\cdot}NO + 4{\cdot}NH_3 + O_2 \rightarrow 4{\cdot}N_2 + 6{\cdot}H_2O$




- Step-response experiments to characterize CI & onset transients
  - Range of temperatures and concentrations
  - 5-Step Protocol to investigate individual & combined half cycles
  - ***Our measurements are the first to resolve half-cycle rate balancing***
- Formulate global SCR model based on the two half cycles
  - CI & transient nature varies with model formulation & kinetic parameters
    - Examples show broad dependence of transient performance on model parameters
    - Model CI trends are consistent with measurements
  - ***Our half-cycle model is the first to show this transient SCR nature***
- Use data to formulate, tune & validate the global SCR model – ***Next Steps***

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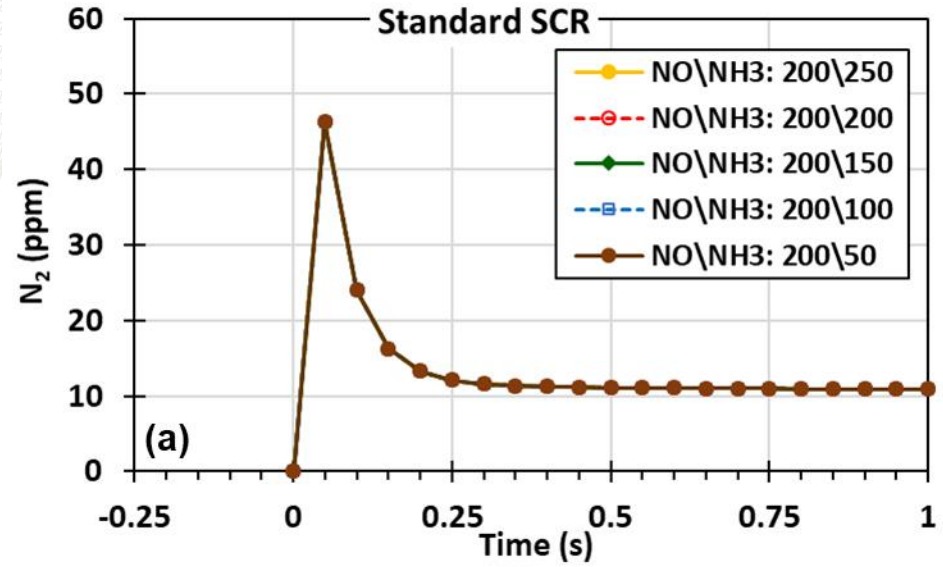
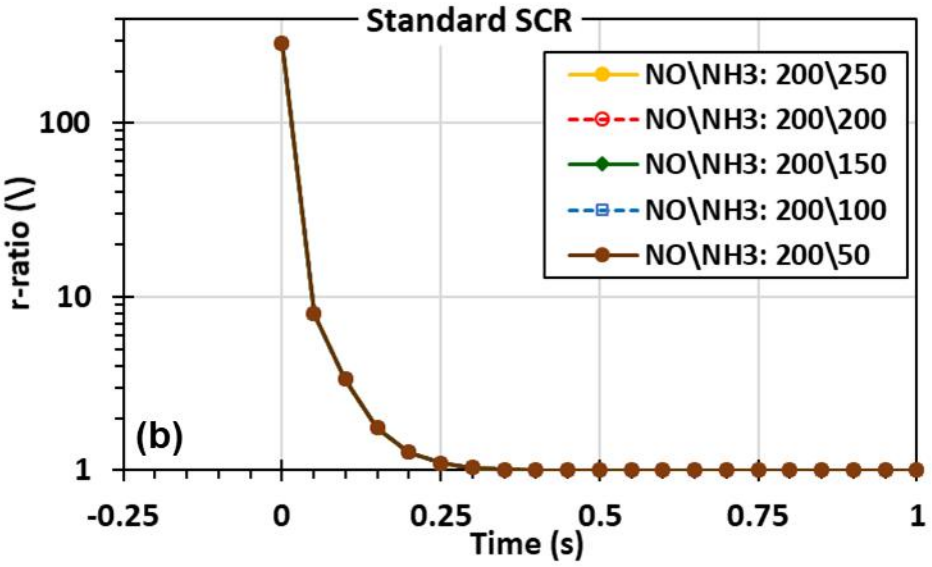
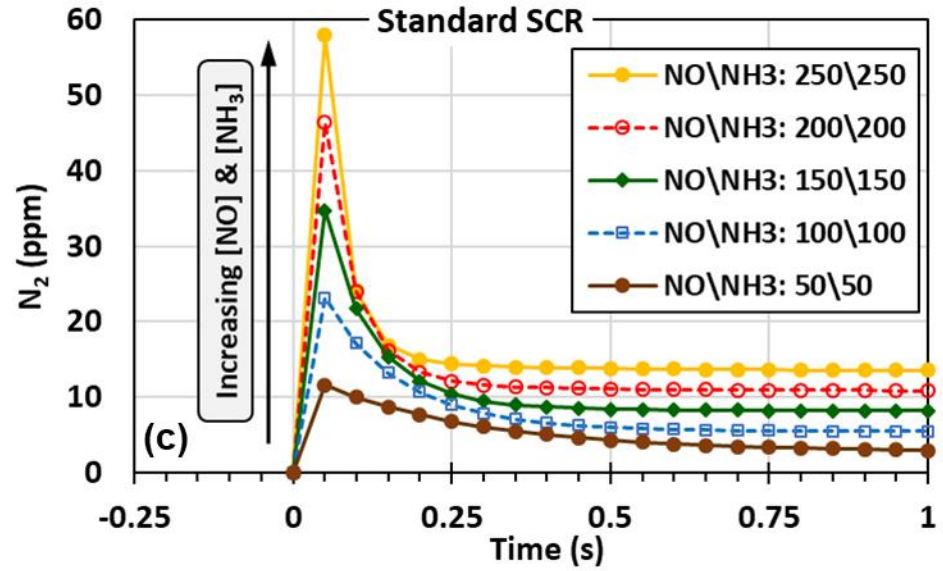
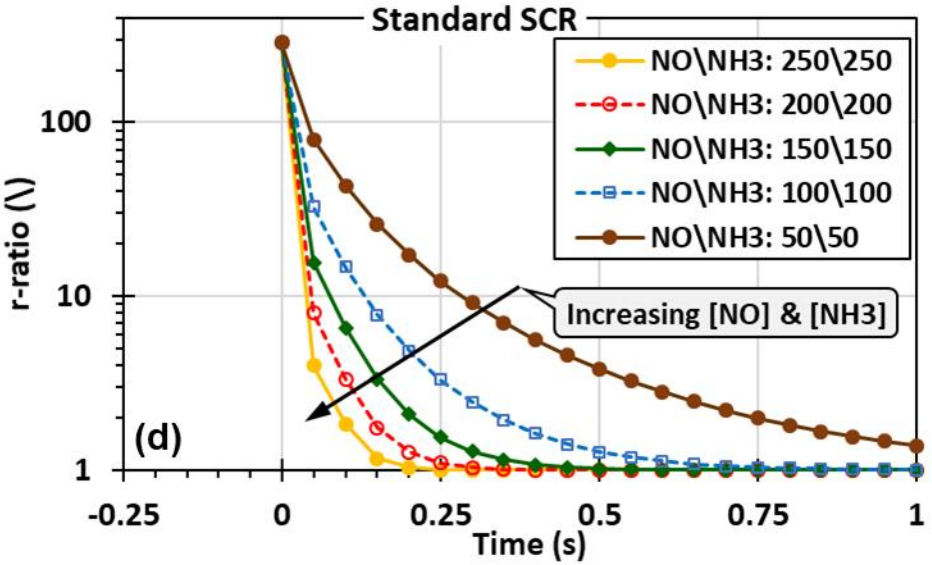
# Global Model – CI varies with [NO] but not with [$NH_3$]



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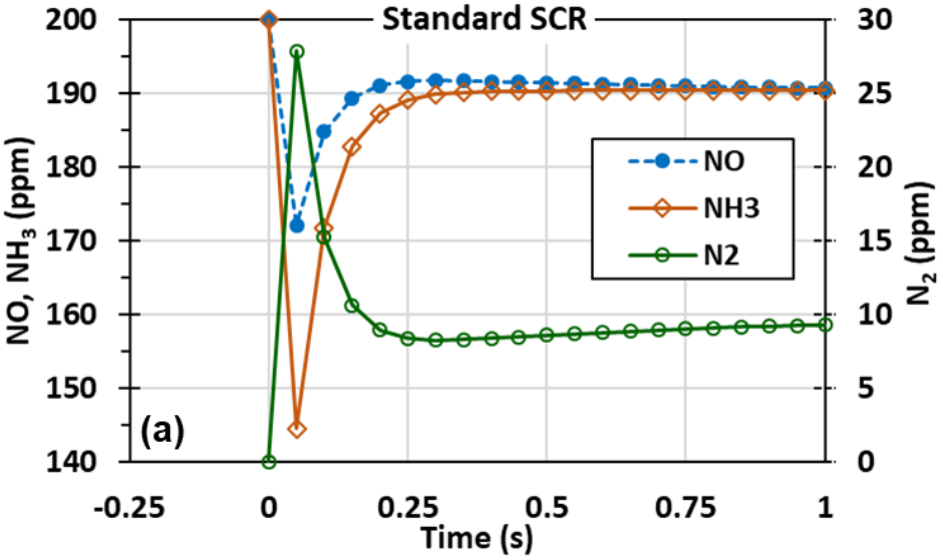
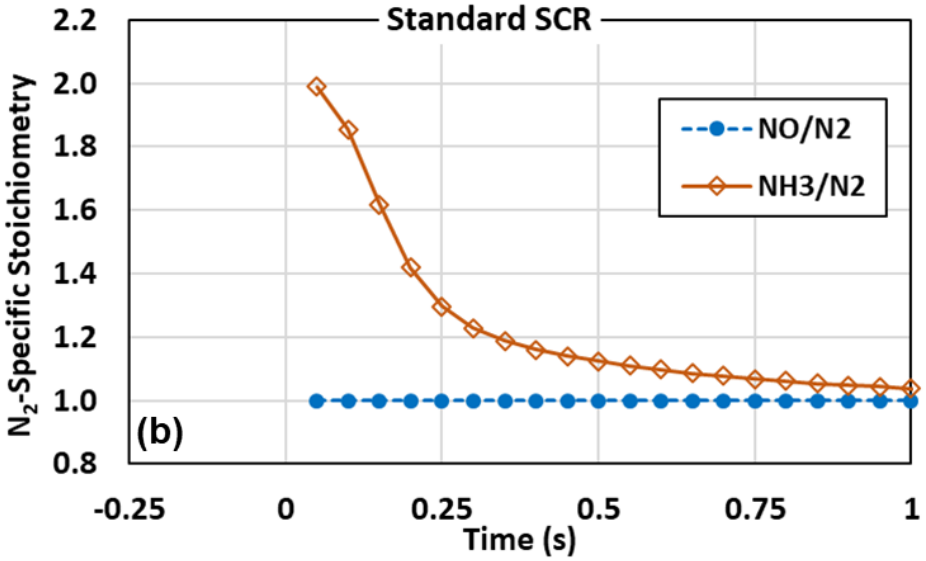
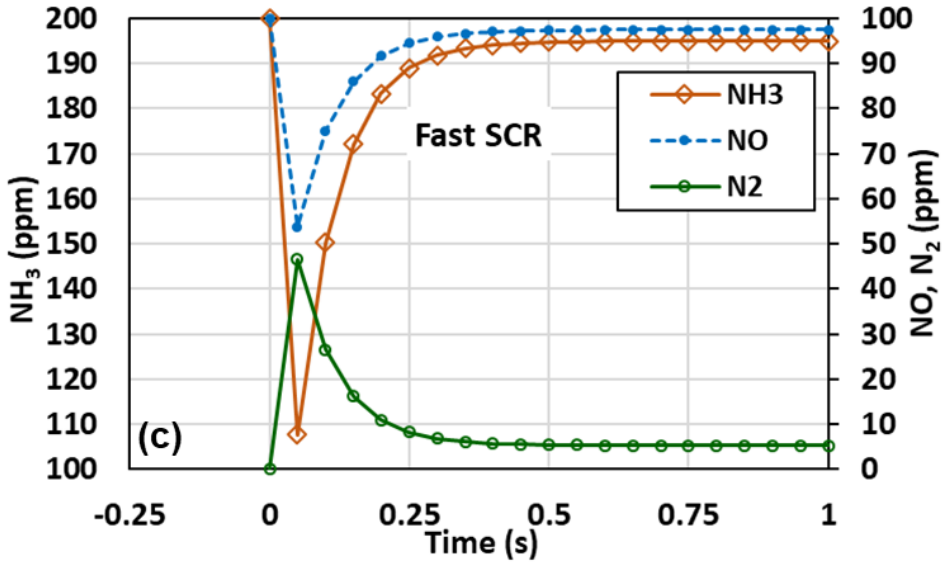
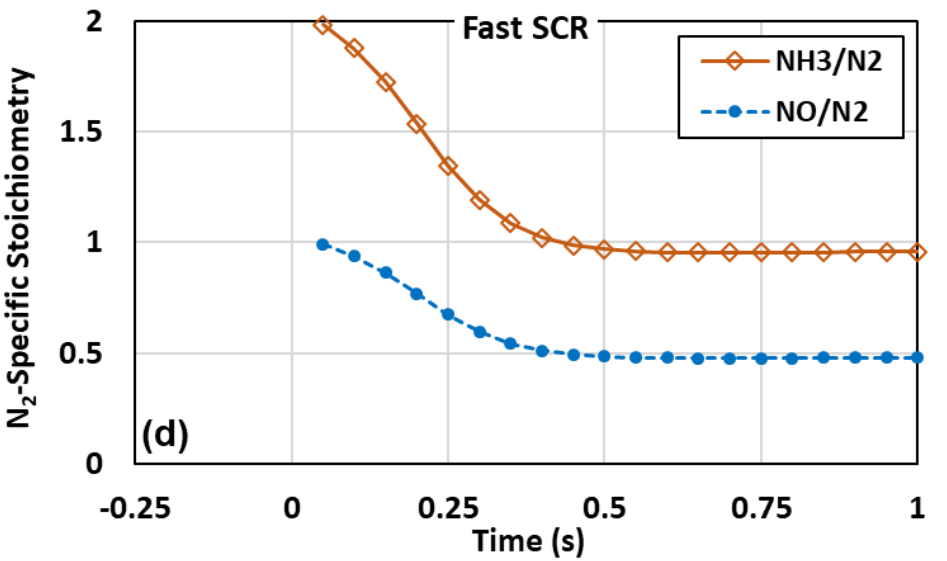
# Global Model – Stoichiometry Varies Through CI Transient



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